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FLEXOGRAPHIC DEINKING WITH ELECTRIC FIELD TECHNOLOGY BY DESTABILIZATION AND FLOTATION

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My Inspiration-
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SUMMARY

Every year, millions of tons of paper are diverted from landfills and recycled. Newspaper constitutes a large portion of total paper recycled, providing a cheap source of raw material for the paper industry. The recycling of newsprint paper involves the separation of ink from the newsprint, which can be done either by flotation or washing. Conventional flotation processes for separating ink are not adequate for newsprint printed using flexography printing technique and with water-based ink. The removal of these flexographic water-based inks by washing is a better alternative. However, one drawback of washing is that it has lower yield. In addition, the subsequent wash filtrate is difficult and costly to decontaminate. The overall goal is to develop a combination of processes that can remove ink from a feedstock that contains up to 100% flexographic ink newsprint.

In the present work the objectives are to (1) demonstrate that incorporating an electric field into a conventional deinking process improves deinking efficiency, (2) propose a mechanism of how incorporating an electric field helps to improve deinking efficiency, (3) demonstrate that an electric field can clarify water containing flexographic inks and identify the mechanism behind electric field clarification of water, and (4) demonstrate that by incorporating electric fields into both the flotation deinking stage and water clarification, the target deinking efficiency can be achieved.

CHAPTER 1 : INTRODUCTION

Deinking is the removal of ink from recycled paper and is generally done either by flotation or by washing. There are a number of steps in deinking. In preparation for deinking, the newsprint is first shredded, soaked and then deinking chemicals are added. The newsprint is then pulped with a pulper or disintegrator; the pulping process causes the paper to be separated into individual fiber (or de-fiber) and the ink to be separated from the fiber. Typical pulping variables include temperature, solid consistency, pulping time, and pulping chemicals.

Once pulping is completed, the pulp slurry is diluted to 1% solids suspension (or 1 % consistency). The suspension is made up 98%-99% water and 1% of fiber. Other paper components like fillers and inks together make up less than 1% of the suspension.

1. Flotation involves the introduction of gas bubbles to a 1% consistency fiber suspension. The motion of the air bubbles causes the ink to float to the top of the slurry as froth. Froth is then skimmed off from the top.
2. Washing involves the use of a screen to separate fibers from ink particles based on their size differences. The inks collect along with fines (very small fibers) in the filtrate, while the fiber collects on the screen.

Conventional flotation processes based on fatty acid chemistry are very effective in deinking newsprint printed with oil-based inks. In certain newspaper market, there has been a shift from oil-based inks to water-based inks. Water-based flexographic inks

provide economic and environmental benefits. The printing quality of water-based inks is crisp. The print has a lower rub off and see-through.[1 2] Water-based inks can replace solvent-based inks that contain hazardous volatile organic compounds. However, the introduction of water-based inks in the waste paper stream has caused problems in flotation deinking mills that use conventional fatty acid deinking chemistry. Small amounts of old newsprint paper (ONP) containing flexographic ink can drastically reduce the brightness and residual ink concentration of recycled fibers. The main reasons for this are:

1. Water-based flexographic inks are alkali-soluble and tend to disperse into very fine particles after conventional alkaline pulping, lowering the brightness of the stock at the pulper;
2. The lack of hydrophobic character of the ink which is necessary favorable ink-bubble interaction during flotation; and
3. The tendency of the fine hydrophilic ink to redeposit on the hydrophilic fibers. The hydrophilic inks are an order of magnitude smaller than oil-based inks.

The objectives and outline of this study are:

1. Demonstrate that incorporating an electric field into a conventional deinking process improves deinking efficiency, as shown in Chapter 5 with a batch setup and in Chapter 6 with a semi-continuous setup. Chapter 2 is a literature review of the current deinking chemistries and technologies used for deinking oil-based and hydrophilic inks are their limitations. Chapter 3 discusses basic principle of an

electrolytic cell. Chapter 4 delineates the equipment setup and experimental procedures.

2. Propose a mechanism of how incorporating an electric field helps to improve deinking efficiency as shown in chapter 6.
3. Demonstrate that an electric field can clarify water containing flexographic inks and identify the mechanism behind electric field clarification of water. This objective is discussed in chapter 7.
4. Demonstrate that by incorporating electric fields into both the flotation deinking stage and water clarification, a close mill may be achieved. This objective is discussed in chapter 8
5. Use a mathematic and empirical model to explain pulping and flotation deinking. This objective is also discussed in chapter 8.
6. Chapter 9 and 10 are the conclusions and recommendations, respectively

1.1 References

[1] Josephson, E., William, Krishnagopalan, A. Gopal, Deinking of furnishes containing flex graphically printed old newsprint. *Appita Journal*, 2005. 58(6): p. 470-474

[2] Jarrehult B., Horacek R, G., Lindquist M., Deinking of wastepaper containing flexography inks, 1989. p. 391

CHAPTER 2 : REVIEW OF PRINTING INK AND DEINKING METHODS

Newsprint quality varies depending on the type of printing process, the kind of paper used to make the newsprint, and the types of ink used. In general, the type of printing process and their respective ink carriers include[1 2]

- Flexographic: water
- Rotogravure : Toluene
- Letterpress : Mineral oil
- Offset: Mineral oil

The flexographic printing process involves the use of flexographic water-based inks. The offset printing process typically involves the use of oil-based inks.

2.1 Flexographic ink behavior

Inks typically consist of pigment, binders, and carrier. Inks with oil carriers are oil-based inks, while inks with water carriers are water-based inks. Water-based ink has water-soluble binders, which bind the ink to the paper during printing. This class of ink is made of acrylic resin binders. The acrylic resins also function as dispersant for the carbon black particle dispersion. The acrylic acid or polyacrylic acid in the ink has carboxylic groups, which are fully ionized at alkaline pH. During printing, the water and other volatile ink components, evaporates. Subsequently, as the ink dries, the polyacrylic binds to the paper.

During deinking, the chemicals, which are introduced during pulping, re-solubilizes the polyacrylic acids on the carbon black particle, stabilizing the carbon black particle dispersions. These dispersions are not amenable to deinking by flotation; the interaction between the hydrophilic carbon black particles and air bubbles are not favorable[3].

In deinking operations these inks inevitably builds up in the waste and water streams. In order to reuse or recycle the water streams, the water has to be clarified. The inks are made of negatively charged carbon black particles. Both the anionic carboxylic groups present on the carbon surface and on the polyacrylic acids attached to the carbon surface are negatively charged. These fully ionized polyacrylic acids extend from the surface of the carbon black particle, when the particles approach each other; there is a steric hindrance to the shrinkage of these extended polyelectrolytes. In addition an electrostatic repulsion causes the negatively charged particles to repel other like charged particles.

A stable dispersion that has both electrostatic repulsion and steric hindrance is referred to as being electrosterically stabilized. The charge or zeta potential of the particle is a function of pH. The flexographic ink dispersion is negatively charged at alkaline pH, but when the pH is neutral and acidic, the carboxylic groups are protonated. Protonation of carboxylic groups on the polyelectrolyte would decrease their solubility in water, and eventually they would precipitate. Zeta potential can be altered by the addition of counterions. The counter ions can reduce the electrostatic repulsion between ink particles. As the electrostatic repulsion is reduced, the particles approach each other and come within the distance where the attractive van der Waals forces become significant.

Eventually, the particles agglomerate and coagulate. The critical coagulation concentration (CCC) refers to the amount of counterions needed to coagulate a stable dispersion. The concentration needed to bring the zeta potential to zero may be different from CCC. If the critical coagulation concentration is more than the concentration needed to reach a zeta potential of zero, the dispersion has steric stabilization.

2.1.1 Summary of deinking technologies for flexographic newsprint and their limitation

A mixture of 30% flexo newsprint, 30% offset newsprint and 40% old magazine was treated in a two-pH stage treatment. The first stage was a flotation stage in acidic conditions. The acidic flotation improves the ISO brightness from 36% to 46%. After thickening and bleaching, flotation is repeated at alkaline conditions. The alkaline flotation improves the ISO brightness from 54% to 61%. 100% flexo newsprint was treated with the two-pH stage treatment. The ISO brightness improved from 35% to 40% at acidic conditions, and from 46% to 55% during the second alkaline flotation stage. 90% flexo newsprint was treated using the two-pH stage, a final ISO brightness of 58%.[4]

In another study[5], 100% flexo newsprint was treated with the two-pH stage process, in the acidic flotation; ISO brightness improved from 35% to 40%, and in the alkaline flotation, it went from 46% to 55%. 100% flexo newsprint was treated with alkaline flotation only, ISO brightness improved by 2% from 26% to 28%. At 26% ISO brightness the corresponding effective residual ink concentration (ERIC) was 4760 ppm.

100% offset newsprint, was treated with the two-stage acidic flotation; 31% to 44% followed by alkaline flotation; 49% to 65% ISO brightness. 100% offset newsprint was treated with only alkaline flotation, ISO brightness went from 44% to 56%. For alkaline flotation only treatment, the 100% flexo newsprint has a lower initial and final brightness compared to the 100% offset newsprint; this is like due to their different ink carriers and binders.

In another study, conventional alkaline flotation deinking was used to treat 100% flexo newsprint; only a 10% reduction in ERIC was reported[6].

Besides the two-pH stage method, majority of deinking technologies is based on using alternate deinking chemicals, i.e. specialty polymers and/or surfactants. Examples of alternative deinking chemicals include, organically modified clay; a combination of nonionic surfactant, a fatty acid and a cationic water-soluble polymer; a proprietary BEROCELL 213 (non-ionic surfactant); a combined polyalkylene oxide and surfactant system. The above-mentioned technologies are discussed in details in the literature review.

The primary objective of this study is to show that incorporating an electric field into any of the aforementioned technologies, especially conventional alkaline flotation deinking, would improve the deinking efficiency.

2.2 Literature review

Strategies to deink flexographic ONP include modification of deinking chemicals, stock preparation, pulping, and the flotation process. Modification of the flexographic ink with better floatability is also a viable alternative. A fundamental understanding of how

stock preparation and pulping affect flexographic ink fragmentation and ink deposition phenomena is needed. Water clarification is an important consideration especially with wash deinking. A water clarification process is needed to prevent the buildup of small, sub-visible ink particles in the water streams of a deinking mill, which adversely affect brightness.

2.2.2 Brightness and Effective residual ink concentration

Brightness and ERIC are the main criterion for deinking efficiency. Pulp ISO brightness is defined as the ratio of the radiance of wavelength 457 nm of a paper specimen made from the pulp sample in question to that of a perfect reflecting diffuser (e.g. magnesium oxide). ERIC is defined as the ratio of the absorption coefficient of the paper specimen to that of ink at wavelength of 950nm.

In deinking mills, the Deinked Pulp (DIP) target goal is an Effective Residual Ink Concentration (ERIC) value of 235 ppm, which corresponds to a brightness of about 58%. [7]

ERIC is a measurement of the ink population that affects brightness. This relationship depends on the amount of ink in the sample and the fiber type. These values can vary drastically throughout the deinking process due to furnish changes. The brightness to ERIC curve in Figure A.1 (Adapted Figure 6 from Haynes work[8]) is for a wash deinking operation[9] with samples collected at several different process points. Included in Figure A.1 is a set of ERIC measurements made for the rejects of a flotation cell. The relation of brightness to the log of ERIC is linear above 500, a discontinuity break occurs at 500, and a second linear relationship for the log of ERIC exists below

500. Data collected for DIP samples from newsprint mills across North America show that for ERIC values below 450 (Figure A.2 in appendix, adapted Figure 7 from Haynes work[4]), a drop of 44 in ERIC equals a one-point drop in brightness[10].

2.2.3 Flotation of flexographic inks

The flotation deinking efficiency is strongly dependent on the physical and chemical properties of the particles to be collected in the froth. The collection of inks in the froth is dependent on the size and hydrophobicity of the inks. Flexographic inks are small and hydrophilic. Dorris et al (1995) investigated the collection of flexographic inks by air bubbles in the absence of fibers[11]. They studied the floatability of dispersed flexographic inks in the absence of fiber and pressate collected from three different furnish mixture. Pressate is the filtrate obtained by passing the pulp slurry through a screen.

The ink particle size was shown to increase as the pH decreases (becomes acidic). Protonation of the soluble acrylic binder was found to cause almost complete precipitation of the binder, a significant loss of surface charge of the inks, and to form carbon black aggregates. The zeta potential decreases, i.e. becomes less negative, as pH decreases. The percentage of floated carbon black particles increases as the pH changes from alkaline to acidic conditions.

The effect of Ca^{2+} ions on the stability and collection of the flexographic ink was also studied. The calcium salt and sodium oleate chemistry is reported to be a good flotation collector for oil-based inks[12]. The presence of Ca^{2+} ions improves the percentage of floated ink to about 50%. The percentage of floated flexographic ink was markedly

improved with the addition of sodium oleate in the presence of Ca^{2+} ions. The formation of calcium soap at higher pH, where the sodium oleate anions are largely in a dissociated form, appears to be a very important factor affecting the rate of flotation of flexographic inks. The concentration of Ca^{2+} ions and sodium oleate used in the study is comparable to those used in a commercial flotation deinking process. Dorris et al. explained that high flotation efficiency of these flexographic inks is not achieved in a commercial process because of the presence of fiber.

Chabot et al. investigated the adverse role of the presence of fiber on flotation efficiency[13]. They looked at two systems, a model and real system. The model system consists of wet lap thermo mechanical pulp (TMP) and flexographic ink. The real system consists of a commercial flexo-ONP. At constant ink concentration, the flotation efficiency of ink decreases with increasing fiber concentration from 0.2% to 1%. The impeller speed in the flotation cell seems to slightly increase deinking efficiency at low fiber consistency of 0.3%, but at high fiber consistency of 0.8%, the effect of impeller speed on flotation efficiency is lower. At fiber consistency of 0.3%, flotation efficiency increased significantly up to a certain airflow rate and then remained constant at higher aeration rates. At the higher fiber consistency of 0.8%, airflow rate had no significant effect on flotation efficiency. Through optimization of aeration rate and shear level in the flotation cell, flotation rate of flexo ink can be significantly improved only if fiber concentration during conditioning and flotation is below about 0.3%. At higher consistencies, the detrimental effect of fibers overrides all other flotation variables. Fibers in an agitated flotation cell may affect the size of the aggregates of ink particles by

limiting their growth or by breaking up larger ink aggregates into smaller ones. Large ink aggregates are critical for flotation efficiency.

Davies et al. used a technique that provides visualization and imaging of ink particles in flows around bubbles to characterized ink adsorption on bubble surfaces[14]. Two flow facilities were developed: a stationary bubble tank where bubbles are held at the tip of a needle in a quiescent fluid and a suspending bubble facility where bubbles are suspended in a carefully controlled down flow of the fluid. The facilities were designed to allow optical studies with high-resolution imaging equipment and processing to visualize and measure particle (ink) transport process at the bubble surfaces and in the surrounding fluid. They observed adsorption of oil-based offset ink on the bubbles, but water-dispersible flexographic ink did not exhibit adsorption on the bubbles in solutions of pH 9 based on fatty acid chemistry[15 16]. Their result is expected because at pH 9, the flexographic ink dispersion is soluble and very stable.

2.2.4 Ink redeposition phenomena

Besides the poor floatability of flexographic inks, these inks have a darkening effect on the fiber during the pulping stage, which is prior to the flotation deinking stage. The darkening effect of flexographic ink on fiber increases with pulping time.

Chabot et al. discussed two types of ink redeposition. A reversible deposition occurs during the thickening stage, and a redeposition that occurs during pulping is considered irreversible. During thickening stage, water is removed from pulp slurry using a screen. The resulting pulp on the screen is described as a pad. Flexographic ink (40

mg/L carbon black concentration) was added to a 1% consistency wet lap of thermo mechanical pulp (TMP), conditioned by stirring the mixtures at a rate of 1200 rpm for 5 minutes at 45^{o}C.The effect of pH, calcium ions, and sodium oleate ions on the deposition on the fiber was investigated. After conditioning, the slurries were washed in a dynamic drainage jar (DDJ). A pad was prepared after conditioning and washing in a DDJ. The stirring during conditioning and DDJ washing were similar to the turbulence in a flotation cell studied in a separate in another study.

An analysis of the pad prepared after conditioning shows that acidic pH causes a dramatic decrease in brightness. However, Dorris et al. (1995) show that acidic pH promotes good ink floatability in the absence of fibers[11]. The acidic pH improved floatability due to formation of large inks aggregates but this large ink aggregates have a tendency to be retained on the pad, darkening the pad brightness.

Alkaline pH and the addition of sodium oleate and calcium ions both have a darkening effect on the pad. At constant sodium oleate, an increase in calcium concentration decreases pad brightness, and at constant calcium concentration, an increase in oleate decreases pad brightness. The retention of ink can be caused by the entrapment of the ink agglomerates in the pulp pad formation after conditioning or by adsorption of the ink agglomerates on the fibers during conditioning. These two mechanisms were not clearly distinguishable from the analysis of the pad form after conditioning.

The subsequent pad formation after the DDJ washing (following conditioning) shows that aggregates of ink particles are not bonded firmly enough on the fibers to withstand the high shear forces. Rather, at alkali conditions, the loss of brightness is

mainly due to the darkening effect caused by alkaline yellowing effect and slightly due to adsorption of ink agglomerate on fibers. Chabot et al. concluded that ink aggregates do not deposit on the fibers during flotation, but rather get trapped in the mat by filtration during sheet (pad) formation or preparation. Thus, deposition of water-based ink on fibers during flotation is not the primary mechanism responsible for the poor removal of agglomerated flexographic inks by flotation.[17]

Ben et al. (1996) have conducted experiments that test commercial flexographic ink deposition during displacement washing of the long fiber fraction of a virgin Kraft pulp.[18] A 0.5% consistency pulp was first conditioned for 10 minutes with diluted ink and various deinking chemicals (e.g. calcium salts and sodium oleate) at a stirring speed of 500 rpm. The mixture was then placed in a specially designed displacement-washing cell and gradually thickened (de-watered) to a final consistency of 10% after which displacement washing was done at a flow rate of 20 ml/min using water containing different chemicals. The washed pad was analyzed for brightness.

It has been reported that calcium and sodium oleate destabilize fiber-free flexo ink dispersion. Electrolytes like sodium and calcium can reduce repulsion between particles and cause aggregation of flexographic ink particles and subsequent deposition of small aggregates on the fiber. Moreover, during the formulation of the mat by thickening, calcium oleate and ink were deposited on fiber surface. SEM micrographs show clusters of ink smaller than 3 μm on the fiber mat compared to greater than 10 um aggregates formed with the same chemicals in a fiber-free system. The destabilization of ink suspensions promotes colloidal deposition of reduced size aggregates as pulp consistency increases during mat formation.

The amount of ink adsorbed during mat formation is larger with calcium salt than with sodium salt as shown by the difficulty of the ink to be eluted from the pad by a displacement wash fluid. These results suggest that when excess sodium and calcium concentrations are each adjusted to comply with the Schulze-Hardy rule, calcium promotes a stronger attraction between ink and cellulose fiber than sodium. In a binary system, the separation factor for Na/Ca^{2+} is in favor of the divalent ions binding more strongly to the fiber.[19]

By chelating calcium ions with EDTA, ink re-deposition during thickening was almost entirely eliminated and any ink left in the mat could effectively be washed out by displacement. On the other hand, application of displacement water containing EDTA to displace already retained ink was found to be only partly successful. The partial desorption of ink pigments with increased superficial velocity indicates that diffusion-controlled mass transfer from stagnant flow regions in the pad (bed) is not significant since one would expect the time dependent diffusion process to elongate the breakthrough curves at high superficial velocities. Instead, desorption is explained as possible if the hydrodynamic shear is high enough to overcome the adhesion forces between the particles and the fiber surface. The EDTA is considered an anti-redeposition agent. The use of an anti-redeposition agent in deinking furnishes containing flexographic ONP has been reported[20 21].

2.2.5 Fiber lumen loading

Ben et al. show that during pulping, flexographic inks are deposited on the fiber lumen[22]. After pulping and hyper washing, the SEM images showed that the external fiber surface and the fibrillated areas of the surface of the pulp were free of redeposit

inks, but inks were located on the surface of the lumen. The lumen-loaded ink particles are protected by the cell wall from dislodgment during pulp processing. Hence, these particles are neither washable nor floatable. Comparison was made between a model system, a mixture of commercial flexo ink and Thermo Mechanical Pulp (TMP) and a real system, 100% flexo-printed ONP. The real system studied had lower ERIC than that of the model system. They explain that there are possibly two reasons for this difference. First, ink particles detached from a flexo print may be larger than in native ink, which, before printing, had a particle size of about 0.1μm. This larger ink size could hamper penetration of ink particles through the pits of the fibers. Secondly, never-dried TMP, which never been dried or pressed, would have lumen not yet collapsed. Inks easily access TMP lumen. Besides these two reasons, flexographic ink, after undergoing printing and drying, tends to be a large particle and thus, will also give lower ERIC. The concentration of ink in the two systems may be different. Lastly, the relative increase in ERIC is higher for a virgin TMP compared to recycled ONP for the same increase in effective ink concentration.[23]

Based on their laboratory study, they proposed short pulping time of 0-2 min. The potential advantage of shorter pulping time is higher pulp throughput, reduced energy cost, and a more flexible strategy for bleaching.

Ciampa [24] studied the effect of pH, surfactant concentration, pulping time and temperature, on re-pulping, flotation and washing. Lowered temperatures, pH, shortened pulping time, showed improvement in deinking. However, surfactant concentration did not show any effect in the process of deinking.

Ciampa also reported an ink redeposition. Blank paper (composed of 25% softwood Kraft and 75% ground wood) was pulped at pH 5, 0.1% commercial surfactant, 25^{o}C and 6% consistency in a bench scale re-pulped at 2900 rpm for 20 minutes, and added previously dried and ground commercial flexographic ink to the pulp (0.015 g/g). The pulp continued re-pulping for another 30 minutes, taking samples at 5, 10, 15, and 30 minutes. These samples were diluted to 0.5% consistency, and then rinsed 15 times in a dynamic drainage jar (rpm –2000) with a solution containing sodium carbonate and a dispersing agent. The brightness of the pulp samples before and after washing was measured. These tests were then repeated with different newspaper ink at a lower ink concentration of 0.005 g/g paper. The results indicate that for both ink types, the brightness loss is greatest during the first 5 minutes of re-pulping but may continue up to 15 minutes after the dried ink particles are introduced into paper that has already been de-fibered.

Nesbit studied the effects of pH, re-pulping time, and re-pulping power on flexographic ink detachment and redeposition on a model re-pulping system.[25] The ink's carbon content determined by Thermogravimetric Analysis (TGA) and brightness was used to measure the degree of detachment and redeposition. Residual ink on pulped fibers is low when the re-pulping at basic conditions, and high when re-pulped in acidic conditions. The ink binder solubility is pH dependent and is not soluble at acidic conditions. Higher re-pulping power is needed in acidic conditions and lower lumen loading is suggested. Langmuir model was used to fit data (adopted from Ciampa's work) from acidic re-pulping experiments during which previously printed, dried, and ground

ink was added to de-fibred newsprint that had not been printed. The Langmuir equation did not fit data collected from the experiment under which printed-paper was re-pulped.

2.2.6 Deinking chemical and surfactant effect on the flexographic inks behavior

Ryu et al. used Oleyl ester and Oleyl ether non-ionic surfactants and an alkaline and neutral deinking process to deink furnish containing flexographic ink[26]. Alkaline deinking was done using 1% caustic soda and oleic acid. Neutral deinking was done using 0.2%, 0.4% and 0.6% nonionic-surfactant (either using Oleyl ester or Oleyl ether). A furnish that consisted of both offset and flexo -ONP was deinked. Deinked pulp brightness was higher using neutral deinking than alkaline because lower darkening as well as greater ink removal occurs in neutral deinking. The deinked pulp brightness decreased with flexo-ONP percentage in the furnish mix. Oleyl ether was a better surfactant and better yield is obtained in neutral conditions than alkaline. The Oleyl ether yield decreased as the surfactant dosage increased. Lower yield during alkaline deinking was attributed to the presence of calcium ions.

Ryu et al. also deinked a separate furnish which consisted of Old Magazine (OMG) and both offset and flexo-ONP. In this case, brightness of deinked pulp was independent of OMG content and pH conditions (i.e. either neutral or alkaline). When the furnish contained OMG, the yield decreases and even more so at neutral deinking condition than at alkaline condition. The deinked pulp freeness and ash removal efficiency is inversely related to the yield. Freeness tends to be decreased by refining and by increasing the concentration of fines in the fiber.

Flexographic ink was added to pulps including Thermo mechanical pulp (TMP), softwood Bleached Kraft pulp (BKP) and hardwood BKP and the brightness reduction after flotation was examined. The brightness reduction was highest with the chemical BKP, the lower brightness of the pulp persists after hyper washing. This indicates that the chemical pulp fibers tend to be contaminated more severely than mechanical pulps with flexo ink particles. The amount of flexo ink deposited onto the pulp fibers was determined by measuring the absorbance of white water. It is evident that the contaminated level of (BKP) is a lot higher than that of TMP and is even higher for refined BKP.

Sain et al. studied the flotation deinking of furnish that contains flexographic ink using various deinking chemistries.[27] The chemistries used were conventional including, calcium and soap, a fatty oil alkoxyl derivative, and a new system designated as a small ink particle agglomerating agent (SIPA) which is a copolymer of an aromatic hydrocarbon, and 2, 5 furandione. In addition, a polyamine polyphosphonic acid (DTPMPA) ink dispersion agent was also studied in the secondary flotation deinking stage of a two-stage flotation sequence.

SIPA particles are neutralized either by lowering the pH or by the formation of Ca-salt. SIPA can adhere to ink particles, which are equal and/or smaller in size, due to particle hydrodynamics. Subsequently, the attached ink-SIPA particle can grow in size by colliding with other particles of similar sizes. These ink-SIPA composites are more resistant to breakage by mechanical action than conventional ink aggregates formed by Ca-Oleate as can be seen from the effect of agitation speed on turbidity of agglomerated ink suspension. These mechanically stable “ink-SIPA composite" aggregates are

hydrophobic and are then attached to air bubbles. This effect is evident from the brightness gain after double stage flotation.[28] . Table 2-1 summarizes the double stage flotation of 100% flexographic ONP and mixed pulp of equal amounts of flexographic ONP, offset ONP, and xerographic furnishes.

Table 2-1 Effect of Chemical composition of SIPA on Double stage flotation* Brightness, % ISO

SIPA Composition	Initial Brightness	Sipa-1	Sipa-4		Sipa-3	
Flotation stage		1	1	2	1	2
100% flexographic ink	34	38	41	47	43	52
Mixed pulp	45	52	54	57	58	62

Cody et al. described an invention that entails forming an Organoclay deinking agent in an aqueous system, contacting ink from wastepaper with an effective amount of the Organoclay deinking agent, and recovering deinked pulp from the system.[29] The invention contemplates five means for forming the Organoclay; first, ammonium salts and cation-exchangeable clay are added to the aqueous system. Secondly, ammonium salts are added to a waste, which already contain cation-exchange clay. Thirdly, the ammonium salts are mixed with the clay, and then an anhydrous blend is added to the aqueous solution. Fourthly, no salts or clay are added, but both ammonium salts and

cation-exchangeable clay are already present in the wastepaper. Fifthly, by adding ammonium salts to the ink, paper sizing or paper before the paper is printed. The ammonium salts are liberated during pulping of the wastepaper, and clay is separately added, so that the clay and ammonium salts react to form the deinking agent. A suitable hydrophobic ammonium salt is methyl trihydrogenated tallow ammonium chloride (MHTAC) and cationic clay, including bentonite and hectorite. The operation is preferably carried out in alkaline conditions.

This organoclay invention was implemented in a flotation deinking pilot-plant.[30] The plant was a 30 tons/day continuous-process pilot plant. Two trial runs were performed in the plant. In trial 1, the furnish composition was 25% flexographic ONP, 45% offset ONP and 30% OMG. The composition for trial 2 was 30% flexographic ONP, 40% offset ONP and 30% OMG. In trial 1, the GE brightness feed flotation was 35.3%, and GE brightness flotation accepts was 50.5%. In trial 2, the GE brightness was 38.6% and 50.5% for the feed and accepts respectively. The deinking chemistry used in trial 1 was 0.2% DPTA, 1.0% silicate, 1% peroxide and 1.0% Lionsorb 951.The pH was adjusted to 10.5 using caustic. Deinking chemistry in trial 2 is similar except that the pH was adjusted to 10 and 1.5% Lionsorb 951 was used. The complete process in the trials consists of a pulper, HD cleaner, coarse screen, primary and secondary flotation, forward cleaner, fine screen, disk filter, and a twin-wire press, in that order. The filtrate from the press is recycled as dilution water. The yield was 90% and 88% for trial 1 and trial 2 respectively.

Other deinking chemistries have been used to aid deinking of furnish containing flexographic ONP. The presence of wood resin acids in a tall oil fatty acid has been

reported to enhance flotation removal of flexographic ink[31]. Condensation products of fatty acids and alkoxylated amines have also been claimed to provide improved flexographic ink removal in flotation.[32] Skaar et al. used a deinking agent consisting of a non-ionic surfactant, a fatty acid, and a cationic water-soluble polymer for deinking furnishes with substantial flexographic ink content. Laboratory and pilot plant tests were performed using 5% and 15% flexographic newsprint in ONP/OMG furnish. Process water could be reused without clarification in these tests. In a lab study, a furnish containing 15% flexographic ONP, with a brightness of 37%, was deinked. A combination of non-ionic surfactant and fatty acid gave a flotation accept brightness of 43% and after washing, a brightness of 48.5%. A combination of non-ionic surfactant, fatty acid and polymer gave an accept brightness of 48% and a brightness of 51% after subsequent washing. After optimizing the deinking chemistry in a laboratory study, Skaar et al, conducted a pilot plant trial and their results are summarized in Table 2-2.[33] [34]. No yield analysis was reported. The yield could not be determined from material balance since only the ash percentage of the feed and float accept were given, but the ash percent of the float reject was not given.

In summary, deinking chemicals could be used either as anti-redeposition agents, to modify the degree of ink dispersion, to induce aggregation of inks,[35] [36] and/or the floatability of the inks.

Table 2-2 Brightness profile (Voith pilot plant)

Flexographic ONP %	*5%*	*15%*
	Brightness (%ISO)	
Feed	38	37
Accept	49	47
Wash	51	49

2.2.7 Aeration and bubble size

Flotation deinking of flexographic ink is very poor. The low flotation deinking efficiency is strongly related to the ink particle and air bubble physcio-chemical interactions.

T.G.M. van de Ven et al, (2001) designed a new laboratory flotation cell, consisting of a flow loop and a flotation chamber[37]. The furnish consisted of newspapers or newspapers mixed with magazines and were pulped using a standard mixture of deinking chemicals. An open centrifugal pump circulated the pulp suspension. The typical fluid velocities are in the range 1-5 m/s. Air is injected in the loop by an air injector step diffuser. The pads prepared from pulp suspensions were analyzed for ISO brightness, ERIC, and particle size using Paprican-Ink Scanner.

T.G.M. van de Ven et al studied the impact of the fluid velocity, the effect of the presence of fiber and fines, and the effect of deinking chemicals on the bubble size distribution.

The impact of fluid velocity was investigated at a constant air fraction of 6% air in tap water (volume of air to volume of water). A velocity of 2 m/s, showed a bimodal bubble size distribution, consisting of small and large bubbles. The reason for the bimodal distribution is likely related to the way bubbles break up in turbulent flow. Only the energy associated with eddies smaller than the bubble are effective in bubble break-up; larger eddies merely transport the bubbles. In turbulent flow, a bubble will be constantly exposed to fluctuating extensional and rotational flows. If the shear forces exceed the interfacial forces, the bubbles will break up, provided the bubble is temporarily in an extensional flow regime. The percentage of small bubbles decreases with increasing fluid velocity, implying less asymmetric (more symmetric) break-up at high velocities. Higher turbulence leads to smaller bubbles and the size of the large bubbles approach that of the small ones. For a pure water system, the average bubble diameter increases with airflow rates.

With the step diffuser air injector, the size distributions obtained at different water flows and airflow rates are identical. They are characterized by a bimodal distribution. The size frequency, however, seems to be slightly different. Also, for lower water flow, the frequency of larger bubbles is slightly higher. The bubble size distribution is affected by the level of mixing energy obtained by the kinetic energy of the water flow. While the water flow constant, the kinetic energy is constant, but the need for mixing energy rises with higher airflow rates because a larger air volume must be mixed in. If sufficient kinetic energy cannot be transformed into mixing energy, the average bubble size will increase.

T.G.M. van de Ven et al. showed that in the presence of fibers and fines, but in the absence of deinking chemicals, the size distribution remains bimodal. Both the large and small bubbles are somewhat larger and the percentage of large bubbles is smaller compared to the water only system. Turbulent energy is likely affected by fibers, which are known to reduce drag. A reduction in turbulent energy would result in a larger probability of asymmetric break-up (unequal bubble size is formed) and thus an increase in the number of small drops was observed.

In the presence of deinking chemicals, the bubble size distribution became unimodal and bubbles were much smaller. This small bubble size was due to a reduction in surface tension by oleate, favoring bubble break-up. The addition of calcium salt forms calcium oleate precipitate, which leads to higher surface tension and larger bubbles.

Doubling the airflow rate showed a slight improvement in the rate of deinking efficiency. However, increasing the fluid velocity causes a greater improvement. This faster deinking is the result of the increase in the number of collisions between ink particles and air bubbles per second, with increase velocity and an increase in the particle-bubble adhesion efficiency. This effect is due to the presence of smaller bubbles, caused by the increase in velocity. The adhesion efficiency depends on the ratio of particle size to bubble size.

The observation that the air volume fraction has little effect differs from the findings of Julian Sanint-Amond[38], who showed that an increase in ink flotation efficiency with increasing air ratio in column flotation.

But Hunold et al. showed that the brightness gain is not always directly proportional to the increase of the airflow rate[39]. Hunold et al. studied various air

injection types used in injector-aerated pilot plant flotation cell including; Model injector (venturi-type injector), Step diffuser, and Pilot injector. The injector design affected the bubble size distribution in water. However, no significant effect is seen in deinked pulp flotation. The model injector improves the brightness faster at the same airflow rate than the other injectors. Different injectors resulted in different efficiencies at the same airflow rate. They concluded that in flotation, not only the volume of air, but also the average size of the air bubbles as well as their distribution is significant.

Julien Saint Amman et al. studied the effect of particle size and speck removal efficiency of the de-inking steps.[40] They adopted a first order kinetics model to discuss flotation theory. They concluded that small bubbles, due to their higher specific surfaces, are more effective than large bubbles but also lead to higher fiber losses for a given air ratio.

Particles in the size range of the visible limit (i.e. about 50 microns) show the highest flotation rate constants. Small ink particles and especially large specks are more difficult to remove. The influence of the consistency increases with the speck size (0.1 mm to 1 mm) but do not affect ink particles flotation.

T.J. Heindel discussed the fundamentals of flotation deinking. For typical ink particles, the Stokes number is very small ($St<<1$) and the inertial forces have a negligible influence on particle motion. So, no direct head to head collision is expected. The interaction between air bubbles and ink occurs by an interception mechanism.

However, only particles that are sufficiently hydrophobic are able to attach themselves to the bubble through the formation of a three-phase contact with a finite contact angle[3].

In summary of the papers reviewed, efficiency of flotation deinking is reduced for sub-micron ink particles and is increased for hydrophobic ink particles and for small air bubbles. Thus, flexographic ink particles, which are hydrophilic and sub-micron in size would be difficult to deink. The air injector type, the bubble size, and the bubble size distribution will affect deinking efficiency of flexographic ONP.

2.2.8 Processes used in deinking flexographic ink

Deinking efficiency can be improved by a combination of processes. For example, the deinking of flexographic-printed paper can be achieved by a combination of flotation and washing deinking. Another form of process modification is the addition of a recycled stream, where flotation rejects are processed and recycled to the feed.

Galland et al. proposed a two stage deinking process, a non-alkaline stage followed by alkaline deinking stage[4]. They demonstrated the advantage of alkaline deinking conditions for deinking offset print (especially aged print) and the advantage of non-alkaline deinking conditions for water-based ink.

The first non-alkaline deinking stage was suitable for flexo newsprint. The difficulties in removing flexo ink in a conventional deinking process are related to ink composition. Water-based flexographic inks contain acidic resin binders (mainly acrylic resin), which become water-soluble or dispersible when neutralized with organic bases such as amines. After printing, the amines are dissipated by volatilization or absorption by newsprint. In conventional deinking, conditions are alkaline, ink binders are solubilized, and very small particles of ink are dispersed into the pulp suspension, which are very difficult to remove. One advantage of neutral deinking is that less anionic trash is produced. Flexo-ONP showed a higher gain cationic demand than offset-ONP when

pulping conditions was changed from neutral to alkaline. Also, less ink dispersion and redeposition occurs at neutral pulping. Ink redeposition was measured by ERIC measurement of hyper washed pulp in both neutral and alkaline pulping. The second deinking stage involved alkaline treatment. Brightness of 62% was obtained after a six hour trial with a furnish mixture of 30% flexo newspaper, 30% offset newspaper and 40% magazines. 58% brightness was achieved with 90% flexo newspaper. However, no ERIC data was reported.

The measurement of pulp brightness is not sufficient to characterize ink detachment because of the yellowing of the pulp when caustic soda is used without peroxide and also because the bleaching effect of peroxide when used with soda. The measure of brightness of the entire pulp and hyper-washed pulp is helpful to compare ink fragmentation and detachment respectively.

In a separate study, Galland et al. investigated a number of processes for deinking furnishes containing flexo-ONP. The processes are conventional alkaline deinking process, alkaline flotation plus acidic flotation process, an alkaline washing and flotation process, alkaline flotation plus three washing stages, and a neutral flotation plus alkaline flotation process developed by the Centre Technique du Papier (CTP). All the processes tested with alkaline pulping conditions have led to low final brightness in comparison to the neutral pulping conditions. At neutral pulping conditions, the ERIC shows less ink fragmentation in the pulping stage and less ink redeposition as observed in the ERIC of hyper washed deinked pulp. The furnish used for this investigation was 40% OMG, 30% flexo-ONP, 30% Offset-ONP. ISO% Brightness ranging from 32% to 62% was reported in the study.[41]

Changes in the pulping process can also affect deinking efficiency. Galland et al. studied the effects of pulping time, consistency, technology, pH, and/or chemistry on ink fragmentation. For each pulping technology, higher consistency gave higher ink fragmentation. Alkaline pulping conditions led to a much more pronounced increase of ink fragmentation. Drum pulper gave lower ink fragmentation than helico pulper even at higher pulping consistency. The ink redeposition phenomenon was reported as an ERIC value as a function of pulping time for hyper-washed pulp. Ink redeposition during pulping is mainly dependent on the ink fragmentation. The ERIC values of pulp after pulping ranged from 2000 ppm to 4800 ppm depending on the pulper type used, pH, consistency and pulping time. The ERIC values after flotation ranged from 1500 ppm to 3800 ppm. Lastly, the ERIC of hyper washed pulp ranged from 250 to 1650.[6] The furnish used in this study was 80% Flexo-ONP (40% British flexo newspaper and 40% Italian flexo newspaper) and 20% unprinted newspaper. Helico pulper had a consistency of 12% and the drum pulper consistency was 15%. The neutral condition used a surfactant and the conventional alkaline condition used fatty acid soap. Their results are summarized in Figure 2-1 and Figure 2-2, which were adopted from Galland et al study[6].

Finally, Greg et al. used an alternative process of flotation. A spray technology was used to increase the deinking efficiency of 100% flexographic ink pulp slurry.[42]

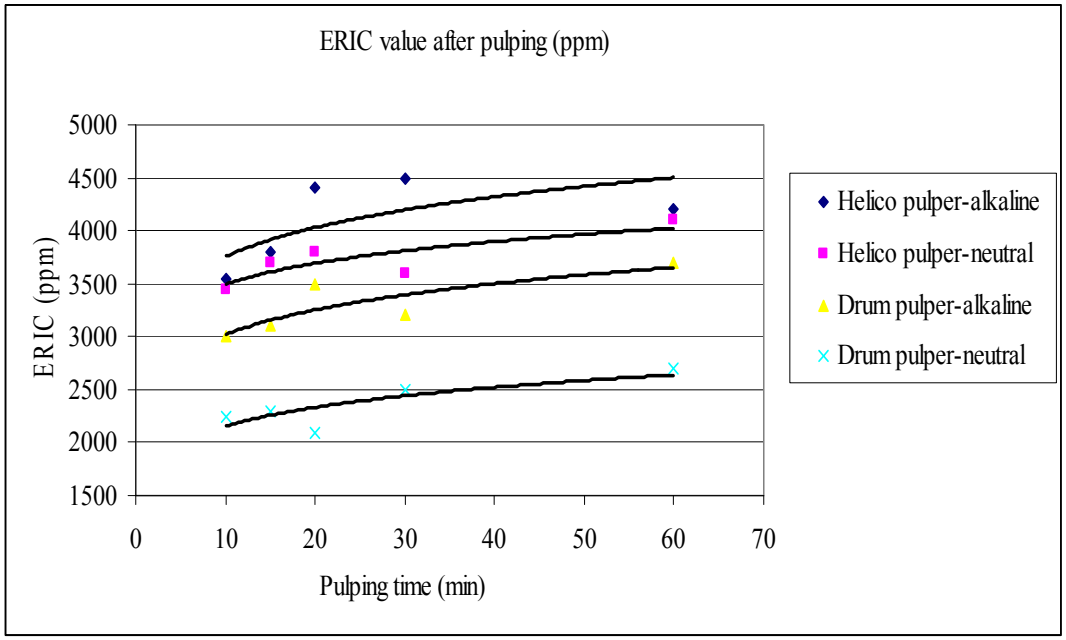

Figure 2-1 Effect of pulping time, pulping consistency, pulper type and pH on ERIC value @ 950nm [6]

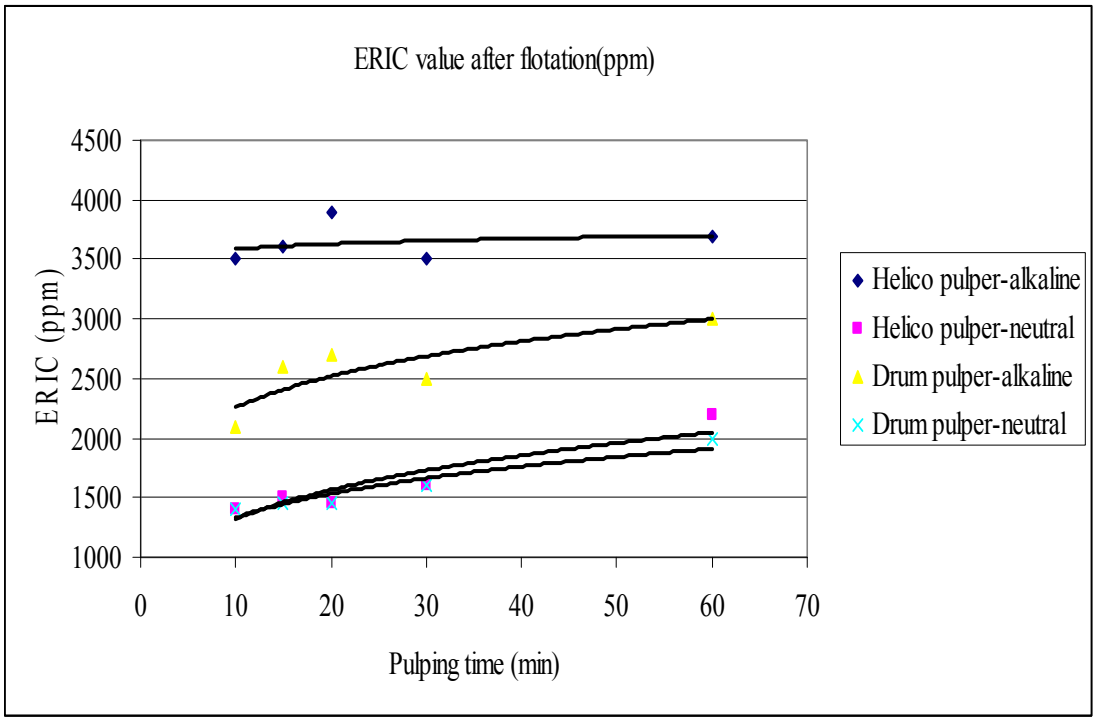

Figure 2-2Effect of pulping time, pulper type, consistency and pH on flotation deinking[6]

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CHAPTER 3 : ELECTRIC FIELD

3.1 Electric field and electrochemical cell

The electric field technology is essentially an electrolytic cell that consists of stainless steel electrodes and electrolyte solution. The electrodes are connected to an external power source that drives non-spontaneous chemical reactions. In an electrochemical cell, the anode is still the location of oxidation, and at the cathode the reduction[1].

Electrolysis of water is the decomposition of water (H_20) into oxygen (O_2) and hydrogen gas (H_2) due to an electric current being passed through the water.

At cathode $2H_20(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ standard potential at 298 K is -0.83V

At anode $2H_20(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ standard potential at 298 K is +1.23

Care must be taken in choosing electrolyte, since an anion from the electrolyte is in competition with the hydroxide ions to give up an electrode. An electrolyte anion with less standard electrode potential than hydroxide will be oxidized instead of the hydroxide and no oxygen gas will be produced. At the cathode, a cation with a greater standard electrode potential than a hydrogen ion will be reduced instead and no hydrogen gas will be produce.

Typical chemicals used in deinking include, H_2O_2, NaOH, Na_2SiO_3, and $CaCl_2$. Ca^{2+} and Na^+ both have a lesser standard electrode potential than a hydrogen ion. However H_2O_2 has a greater standard electrode potential than hydrogen ion and will be reduced, until it is consumed. At the anode, SiO_3^{2-} is less than the standard electrode potential of hydroxide and is oxidize, until it is consumed. The Cl^- is not less than the

standard electrode potential of hydroxide ions but will be oxidize if there is over-potential.

The premise for using an electric field in de-inking water-based inks is based on the fact that a process called electro-flotation has been employed in the removal of suspended particles from effluents. These suspended particles are normally less than 20 μm and have close to neutral buoyancy. Empirically, very small bubbles, often less than 100 μm in diameter, can be used for the removal of fine particles. One of the methods to accomplish this aim is electro-flotation in which bubbles are generated by electrolysis[2]. The removal of fine (<13μm) particle is high using bubbles of the order of 50 μm in diameter and do not require surface hydrophobicity.[3]

Decomposition of pure water into hydrogen and oxygen at standard temperature and pressure is not favorable in thermodynamic terms, as half of the reaction's standard potential is negative values. Thus energy supplied by an external electrical power source is needed

If the anode electrodes are aluminum or copper instead of stainless steel electrodes, the follow chemical reactions occur in addition to the generation of hydrogen and oxygen gas bubble been generated.

$Al^{3+} + 3e^- \rightarrow Al$ -1.66V

$Cu^{2+} + 2e^- \rightarrow Cu$ 0.34V

If the potential difference between electrodes is greater than the standard potential of the metal, the reactions will occur. The polyacrylic acid binder of the flexographic ink reacts with metal ions released from the anode electrodes in a process called electro-coagulation[4].

The entire electrochemical series potential range is ±4 Volts. However, a greater potential may be required to drive the electrochemical reactions since the process is not 100% efficient.

Electric field and flotation

Krodel proposed a method that incorporates the electric field into the pulping process of waste paper.[5] Makris et al. introduced an electric sparking technology to improve deinking efficiency of a 20% OMG/ 80% offset-ONP.[6] These technologies were not applied to furnish containing flexo-ONP. Jahandah et al. proposed a new method of flotation deinking using a direct current. They showed a reduction in the chemical consumption in the deinking process by using the present method and apparatus. The applied DC electric field also will dissociate the deinking chemical, thus increasing the efficiency of the deinking process. The patent reported a better change in the number of specks for old newsprint, old directory, yellow pages, white papers, old catalog and office waste. But it is questionable at 2.5% sodium hydroxide[7]. Based on these results, BaOsman et al. studied deinking of various furnishes including 100% flexographic ink ONP[8]. However, BaOsman et al used a Lawson tube in combination with an electric field[9]. BaOsman did not investigate flotation deinking only, separate from wash deinking. So the electric field effect impact on flotation deinking only is not delineated.

3.2 Process water clarification

The concentration of small, sub-visible ink particles that have a negative effect on brightness can buildup in the recycled mill process water if these ink particles are not

removed efficiently in the water clarification process[10]. Wastewater generated from deinking mills could be treated and reused. The well-known treatment methods include dissolved air flotation and sedimentation[11.] Dissolved air flotation (DAF) and sedimentation both require the use of chemicals as flocculants and coagulations.

The two-polymer system relies on 1) a low molecular weight polymer (coagulant) with a high cationic charge that neutralizes the charge of the anionic contaminant, and 2) a low anionic charge density polymer (flocculants) with a high molecular weight, which forms floc by a bridging mechanism. An effective DAF process for water containing dispersed flexographic ink particles involves the addition of a vinyl amine containing coagulant followed by a high molecular weight polyacrylamide.[12]

DAF is used to purge flocculated ink and contaminants from the process water for reuse in deinking mills. The objective of DAF is to remove all the suspended solids with air bubbles. This objective is achieved by providing relatively quiescent conditions and small diameter air bubbles (about 0.01 to 0.1 mm). These small bubbles are obtained by dissolving air at high pressures followed by release of the pressure.

Ultra-filtration and membrane separation have also been used to treat wastewater generated from plant deinking flexographic newsprint[13]. The use of electrochemical cells to decontaminate water and wastewater has been reported. However, a study of the uses of electrochemical cells, specifically for decontaminating waste generated from flexographic newsprint deinking, has not been reported. Studies show that electrochemical cells are not always effective in Chemical Oxygen Demand (COD) reduction for all kinds of wastewater[14]. Therefore the use of electrochemical cells has to

be examined for each water and wastewater source. Electrochemical treatment of ink is in the literature.[15] [16]

This present study focuses on the various parameters of electrochemical cells on decontamination efficiency of flexographic ink wastewater. The parameters include the current density, treatment time, and electrode type.

3.3 Electric field in flotation deinking and water clarification

Conventional flotation deinking mills were designed to deink oil-based offset ONP and OMG. An introduction of as little as 5% flexo-ONP into the furnish may upset the deinking operation because the flexo inks are hydrophilic and sub-micron size, with an average size of 0.5 microns as opposed to hydrophobic inks, which have an average size of 20 microns. Feed furnish that does not contain flexo-ONP has, on average, 45% brightness and ERIC of 1200 ppm and an after flotation brightness of 57%.[17] [18] Skaar et al. reported that in a lab study, a furnish containing 15% flexographic ONP, had a brightness of 37%. Galland reported that a furnish containing 30% flexo-old newspaper (ONP)/30% offset-ONP/40% old magazine (OMG) had an after pulping ISO brightness of 37%. Galland also reported that a 100% flexo–ONP had a feed ERIC value of 2000 ppm for acidic pulping and as high as 5000 ppm for alkaline pulping conditions. After flotation, the accept ERIC values were 1500 ppm and 3500 ppm, respectively.

In deinking mills, the Deinked Pulp (DIP) target has an ERIC value of 235 ppm. The 235 ppm ERIC value corresponds to a brightness of about 58%.[19]. Reaching the target ERIC 235 from a starting ERIC of 5000 ppm could be challenging. In order to cope with a 100% flexographic-ONP feed, a combination of treatment methods are

proposed. First in the flotation deinking, an electric field technology is incorporated to improve the deinking efficiency. Thereafter, the stock is screen-washed and the filtrate is subsequently treated with an electric field process called electro-flotation. The water treatment requires no addition of chemical or external gas bubbles. The clarified water can be recycled back into the water stream of the deinking mill.

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CHAPTER 4 : EXPERIMENTAL PROCEDURE

This chapter discusses the major equipment used in this study and the experimental procedures are outlined.

4.1 Equipment Section

Power source

The High voltage regulated power supply is manufactured by Knight Power. It has can deliver a maximum of 10000 volts and its maximum current is 603 milli-ampere.

Pulper

Pulping is a defibering process that converts paper into individual fibers. Pulp disintegration is a three-way operation, consisting of agitation by bulk motion, mixing of the slurry and dispersion by reduction of the solid particle size. The objective is to obtain a homogenous slurry that can be pumped; and to separate contaminates, ink particles and fibers[1].

Two types of pulping were used in this current work.

1. *Hydropulper.* This pulper is manufactured by Adirondack machine corp. it consist of a tank, rotor equipped with blades to induce shocks on contact with the pulp. The rotor speed is 1725 rpm. It is suitable for pulping at low consistency. Volume capacity is 8 liters.
2. *Planetary mixer*. This mixer is not yet used in the pulp and paper industry, it has found application as a pulper on a laboratory scale. Defibering is based on application of heavy impact forces uniformly distributed between the impeller and tank wall. The continuous change of impeller position (planetary motion) means the motion of the

pulp suspension differs from the hydropulper. This allows disintegration of ONP up to consistency of 20%. The high consistency increases friction between the fibers in the overall volume of the tank, not just around the impeller.[2] The planetary mixer used is the Kitchen Aid Mixer, Model K5SS. It has a volume of 4liters, and the rotor speed can vary from 200 rpm upwards. The impeller used was a flat beater.

4.1.1 Semi-Continuous flotation

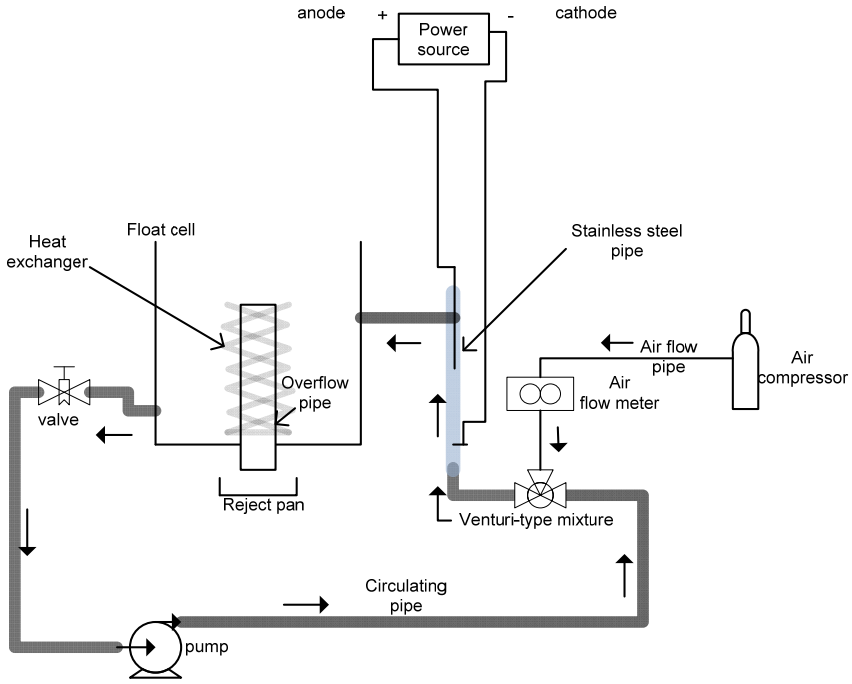

Figure 4-1 Schematic of semi continuous cell floatation cell

The float cell (see Figure 4.1) is made of an unbaffled 8-inch diameter polyvinyl chloride (PVC) pipe, and has a maximum volume capacity of 4.4 L. It is one-foot high. To perform a float experiment, the pre-weighed pulp slurry is poured into the float cell. The circulation pump and the airflow are turned on. When electric field is used, the power supply is turned on. The pulp slurry continues to circulate in and out –through a ¾" diameter and 6 feet long circulation pipe – of the float cell. The stock also flows through the 3/4" diameter, 6" long stainless steel pipe that constitute the electrolytic cell. In the meantime, in the float cell, the pulp slurry in the float is kept at a constant level and froth typically gathers on top of the pulp slurry and eventually overflows through the overall pipe- 3.5" diameter, 7" high. It is collected as reject in a pan placed below the setup. The float cell is equipped with heat exchange for temperature control. In some cases, water was continuously added to the float cell at a rate of 40 mL per minute to assist in the overflow of froth rejects. The added water keeps the stock slurry level in the flotation cell. Froth causes water loss, which reduces the level of stock slurry in the flotation cell. Float studies have been carried out using similar float cell[3 4 5.] However the studies in the literature do not have electrolytic cell in the circulation piping and the air injector used is known as a step diffuser.

Air Injector, Air Flow Rate, Bubble Size, Aeration Ratio

The air source is from an air compressor and the flow rate is varied from 2-10 ft^3/hr. The air is introduced into the pulp slurry through a Mazzei® air injector (Model 784) connected to the circulation piping. The differential pressure drop between the inlet and downstream outlet pressures of the injector controls the suction capacity of the air

injector. The bubble size has not been estimated. But the bubble would coalescence the further away the downstream outlet is. The venturi-type injector provides very efficient mixing between the air and pulp slurry.

The aeration ratio is the product of airflow rate and flotation time divided by the volume of suspension in the cell.

For a given stock volume, a given aeration ratio can be obtained in two ways; either by adjusting the flotation time or the air flow rate. If the airflow rate is reduced accordingly, it is possible to have flotation treatment for a longer time and still obtain the same aeration ratio used in a typical bench scale deinking practice. Short flotation time of 6-12 minutes is usually reported in bench scale operations and a high flow rate of 20 ft^3/hr.

Turbulence Volumetric Flow Rate

The stock is pumped into the cell and it flows in a tangential or rotational direction, in a circular path around the cell. The speed of the rotational flow in the cell and the degree of turbulence is controlled by the circulation pump speed and the air volumetric flow rate. The stock pressure as it circulates is 7.5 psi. The circulation volumetric flow rate is 16 L/min. The Reynolds number was kept constant for most of all experiment performed. (Diameter, 0.01905 m; velocity 0.936 m/s, assume density and kinematic viscosity of water). The Reynolds number is calculated to be $1.78 * 10^4$, indicating that the pipe flow is fully turbulent.

4.1.2 Batch Setup

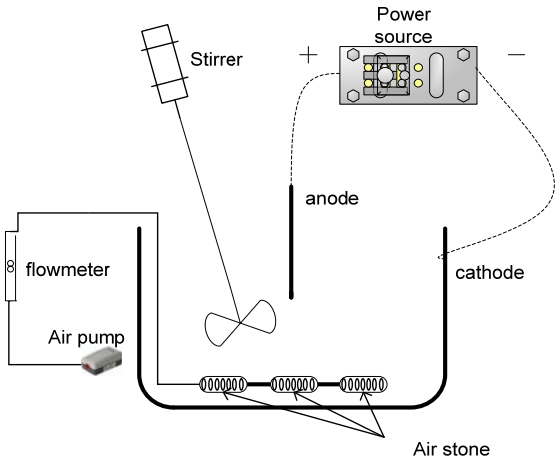

Figure 4-2 Schematic of a batch flotation deinking setup incorporating an electric field.

Batch Setup Description

The batch flotation cell (see Figure 4.2) consists of an unbaffled cylindrical stainless steel container. The cell has a capacity of 4.0 L. Its diameter is 17.2 cm. Conditions for flotation in the cylinder container are as follows: pulp consistency, 1%, the volume of ONP/OMG pulp mixture treated was 3000 mL.

The electric field assisted deinking setup consists of a power source (with positive and negative terminal), and the flotation cell. The positive terminal is connected to the shaft of the stirrer while the negative terminal is connected the flotation cell wall. In some

instance the positive terminal is connected instead to a stainless steel rod placed in the center of the flotation cell. The steel rod is 1/16" in diameter and 8" long. The rod was placed 2" from the bottom of the float cell. Because this cell is not normally used in the industrial bench scale deinking practice, some trials were performed to determine the functionality of the device. A preliminary study was performed to demonstrate that float cell gives comparable deinking efficiency with other deinking study in the literature. The results show the brightness obtained after flotation with the flotation cell is comparable to the values in the literature. The distance between the centrally placed rod and the cell wall is the radius of the cell.

Air Bubbles

Air bubbles were introduced by pumping air through ceramic air stones. The air pump, OPTIMA®, is manufactured by ROLF C. HAGEN (U.S.A) Corporation. It has maximum air output capacity of 5000 cm^3/min. The air stones are manufactured and distributed by Aquarium Pharmaceuticals, Inc. under the name Micro-Bubbler ™. The Micro-Bubbler Ceramic air stone are cylindrical shaped with perforated 1/8" thick wall, which produces clouds of ultra-fine bubbles. The air stones are 2" long and 3/8" in diameter. The air is pumped into the opening in the middle of the air stones and escapes through the perforated walls, forming bubbles.

These bubbles are different from the gas bubbles generated by the electrolysis of water. The volume and size of gas bubbles generated from pumping air through the air stone are larger than the bubbles from electrolysis. A total of 8 air stones were used.

Stirrer

The stirrer is used to provide uniform mixing of the stock. The stirrer used was Stir-Pak® laboratory mixer, Model 4554-00. Barnant Company, a division of Cole-Parmer Instrument. Comp., manufactures it. The mixer speed varies from 500 to 10,000 rpm. The mixer includes: A 3/8" diameter X 12"L 316 SS shaft, and a 1.5" diameter 316 SS three-blade propeller. The shaft was aimed off center to avoid vortexing and to allow strong top-to-bottom turnover. The stirrer is placed in the cell and is 2 inches from the bottom of the cell. The stirrer was set at 1000 rpm (16.7r/s). The stirrer provides and promotes the mechanical impact between the bubble and ink particles necessary for good flotation. The Reynolds number from the diameter and peripheral speed of the impeller using the equation[6] $N_{RE} = \frac{D_a n \rho}{\mu}$, was used to calculate the. D_a is the diameter of the impeller (four pitched blade turbine), 0.125ft, n is 1000r/m (16.7r/s), ρ is density of the suspension, 62.5Ib/ft^3, μ is viscosity of the suspension. N_{RE}=2.4*10^4. The flow is fully turbulent.

4.2 Procedures for Preparation and Analysis of Handsheets: (Following T218 om-91)7

1. Scope

This method describes the procedures using a Buchner funnel for preparing, for reflectance testing, 3 gram specimen sheets of deinked pulp as received, and after hyperwashing. The sheets are made at a pH of 5.0 ± 0.1.

2. Summary

Handsheets are made of deinked pulp received from the mills and hyperwashed pulp. The pulp slurry is adjusted to a pH of 5.0 ± 0.1 using 10 percent acetic acid and the sheet is

formed in a Buchner funnel. The sheet is pressed and dried under controlled conditions to produce a reproducible surface for reflectance testing.

3. Equipment

1. High-speed mixer with two-fixed ripple-edge stainless steel mixing blades, on a stainless steel shaft, and fitted with a square shaped 1000 ml stainless steel canister.
2. Balance, capable of weighing to the nearest 0.1 gram.
3. Graduated cylinders - 1000 ml
4. Filter Paper - 150 mm white filter paper, fast draining (VWR Brand No. 417), Particle Retention-40 mm, flow ate-fast, Catalog Number 28313-104.
5. Buchner funnel, ~ 150 mm inside diameter
6. Water - , preferably at pH 6.0-7.0
7. Press template
8. Drum dryer
9. Drying Plates
10. Blotting paper
11. Acetic acid at 10%
12. 1ml of Alum at 12%
13. NaOH at 0.1 M
14. pH meter

4. Sampling

An objective of this project is to measure the amount of ink remaining with the outgoing pulp that could have been removed, or the free ink. Another objective of this project is to determine the amount of ink that has attached to the fiber and cannot be removed. A deinking operation seeks to do everything possible to minimize the final ink content. Therefore, the best sample location for evaluating how well ink has been removed is at the final deinked pulp (DIP) sample point.

5. Test Specimens

- Determine the amount of deinked pulp needed to make a 3 gram handsheet (based on T240 om-93).[8]
- Based on an approximated consistency collect a two gram pulp sample.
- Dilute to approximately 0.5% consistency
- Place a previously dried, tared filter paper in the Buchner funnel, moisten with water,
- Then apply suction to the flask and filter the slurry. If filtrate is cloudy, refilter through the same pad until clear.
- Remove the resulting pad and filter paper and heat on a dryer. Weigh the paper and pad.
- Replace on dryer. Make successive readings until a constant weight is obtained.
- The percent consistency of the specimen is then:

- % cons. = {[Weight of dry pad & filter paper - weight of filter paper]/ weight of Original pre-filtered sample}*100
- For each condition, original deinked pulp sample and hyperwashed pulp, two handsheets, weighing 3 g will be prepared.
- Weigh out two separate portions of pulp equivalent to 3 grams ± 0.2 of moisture-free fiber.

6. Procedure

1. Dispersion

Disperse with a high-speed mixer, add 3 g of pulp, dilute to 500 mL with de-ionized water and disintegrate at 13,000 rpm for 2 minutes. Measure the pH and adjust to a pH of 5.0 ± 0.1 with acid or base. Transfer to a graduated cylinder and dilute to 1000 mL using de-ionized water, which has been adjusted to pH 5.0 ± 0.1. For pulp containing high amount of flexographic ink, 1ml alum at 12% may be added to reduce two-sidedness and to keep the ink from entering the filtrate.

2. Sheet Formation

Form the sheet on a leveled and fritted glass Buchner funnel. Place sheet of 150-mm filter paper in the funnel, wet it with de-ionized water from a wash bottle, and apply momentarily supply suction in order to seat the filter paper. Make certain that the funnel is level by pouring a little more water over the paper and noting that it disappears simultaneously over the entire area.

With no suction applied to the funnel, rapidly pour in 1000 mL of stock. Apply suction at 15 inches of mercury, and continue until the excess water is removed. Break vacuum immediately. After transferring the sheet to the press, form the second sheet from another 1000 mL of prepared stock.

3. **Couching**

Invert the Buchner funnel over standard blotter paper and, by blowing into the funnel stem, deposit the test sheet and its filter paper on the blotter paper. The blotter paper is located on a flat surface.

Cover with another blotter paper and then the flat couch plate. Place the couch roll gently on the middle of the plate. Rotate the roll backward and then forward five times in 10 ± 2 seconds, with no pressure being applied except for the weight of the roll. The roll should come within less than 5 mm of the edge of the plate each time. After the fifth forward rotation, rotate it back to the middle and lift off.

Remove the couch plate and top blotter, and set aside. Use an indelible pencil to identify the test sheet. For laboratory trials, the test sheet can be allowed to air dry before the optical measurements are taken. Pressing and drying in the following sections are optional.

4. Pressing

Lay a piece of blotter on the press to serve as a cushion. Lay a clean drying plate, polished surface uppermost, on the blotter and center it with the press template.
Place the test sheet face down onto the drying plate with the filter pad on top. Cover with two sheets of blotter paper. The stack from the bottom will then consist of one blotter,

drying plate, test sheet, filter paper, and two blotters. Add a clean plate for the next sheet and center it.

Continue to assemble blotters, plates, and test sheets in the press until four pairs (8 test sheets) have been accumulated. Cover the top with two blotters. Put on the cover of the press and tighten. Raise pressure, as indicated by the gage, to 50 psig. This is equivalent to approximately 350 kPA on the sheet, in 30 seconds from the time the needle begins to move and maintain this pressure for 90 seconds. At the end of that time, release the pressure and remove the press cover.

5. Drying

- Remove the stack of blotters, plates and sheets from the press.
- Remove the filter paper from the test sheet. This prevents bonding during the drying process.
- The handsheets are dried using a commercial drum dryer.
- Conditioning - the handsheets was left at least overnight in TAPPI humidity and temperature-controlled environment until analysis.

6. Measurement of ERIC, ISO Brightness, and Lignin Content with Technidyne Unit

- Both top side and bottom side - Six measurements was made on both sides of each handsheet pad for an average of 12 readings.

7. Ink Scan of Handsheets with Optest's Inkscanner

- Ink scan was used to evaluate ink particle distribution from 10 micrometers to 200 micrometers. Bottoms side and top side –Ten measurements was made on each side of the two handsheet pads for an average of twenty readings.

4.3 ERIC (Effective Residual Ink Concentration)

Paper brightness has been used as product specification of recycled papers. However, the brightness measurement has deficiencies in quantifying ink-removal efficiency, and the amount of residual ink in deinked pulp. Paper brightness depends on additional factors, such as pulp refining, pressing calendaring, formation and bleaching. Jordan and Popson[9] developed a near infrared reflectance technique to measure residual ink concentration in paper made of deinked pulp using Kubelka-Munk theory.[10] The technique has been adopted by TAPPI as Provisional Test Method T 567 pm-97 to measure ERIC of deinked pulp[11]. The technique measures the reflectance at 950nm from a paper sample over a black backing, R_o and reflectance from a thick stack of paper from the same sample, $R\infty$. The Kubelka-Munk constant *k*, the specific absorption coefficient of the sample, can be calculated from the two measured reflectance values, R_o and R_∞.

According to Kubelka[12 13], the specific absorption coefficient is

$$k = S\frac{(1-R_\infty)^2}{2R_\infty} \qquad [1]$$

Where

$$S = \left[\frac{R_\infty}{w\left(1-R_\infty^2\right)}\right] In\left[\frac{1-R_o R_\infty}{1-R_o / R_\infty}\right] \qquad [2]$$

S is the specific scattering coefficient, and *w* is the basis weight. The ink concentration is directly related to the residual ink concentration in the paper sample. ERIC is the residual ink concentration determined as the ratio between the specific absorption coefficient, *k*, of the deinked paper and the absorption coefficient of black ink, k_{ink}. Neglect the absorption by lignin and dye at infrared wavelengths greater than 950nm.

$$ERIC = c_{ink} = \frac{k}{k_{ink}} \times 10^6 \left(ppm\right) \quad [3]$$

Where k_{ink} =10,000m^2/kg, a default value, and the Kubelka –Munk coefficient k is determined from two reflectance measurements using Equation (1).

The ERIC value is based on the absorption of infrared light at 950 nanometers as measured by reflectance and depends on the amount of light scattering due to the sample fiber. ERIC is a function of the ink size, the level of ink dispersion or agglomeration, ink concentration and type of ink on the recycled pulp. Ink has distinctive absorption of infrared light from lignin and dye and other colorants. The ERIC value is a measure of the overall darkening effect of remaining ink, not the actual amount of that ink. Consider two pieces of paper, both of which contain the same amount of residue ink. In one case all of the ink is agglomerated into a few large blobs. In the other case the ink is broken

down into small particles, and is uniformly dispersed throughout the sheet. The later instance would have a higher ERIC value because individual ink has a higher surface area and its light absorption characteristic nearly maximized. The ERIC value is affected more by small size particles less than 3 microns.

Leighton and Miranda[14] showed that carbon black deposited in paper with a constant concentration but different speck size produce very different brightness levels. The technique works fairly well except for the large standard deviations encountered in measuring papers of high opacity resulting from high basis weight, ash content, or ink concentration (high ERIC values). For opacities above 97%, average $\bar{S}$ value is used instead, for scattering coefficient based on the idea that the scattering should not be expected to change in a sheet as absorption changes. This approach removes the logarithmic singularity when $R_o=R_\infty$

However, determination of the best value for *S* in a sampling of recycled newsprints was found to be uncertain by about 10%. When comparing specimens from different mills, it would be advisable to calculate both the absorption and scattering coefficients. Specimens from the same mill may also differ in scattering coefficient if the fines retention or filler content changes in the deinking process.

Vahey et al, proposed an alternative approach, RT method, which avoids the uncertainty inherent in the approximation by applying the KM theory to the measurement of diffused refection (R) and transmission (T) in single sheets.[15,16]
The ERIC coefficient of variation (COV) was determined for each test methods; the RT method had the lowest COV at ERIC 2700. The corresponding ERIC COV first exceeds

that of the $\bar{S}R_\infty$ method when ERIC is about 5000ppm at which point the COV was 11%. At 1000 ppm the COV was 8% and 16% for RT method and $\bar{S}R_\infty$ method respectively. A method $R_o R_\infty$ is similar to $\bar{S}R_\infty$ but is only valid for sample with opacity less than 97%.

4.4 Thermo gravimetric analysis (TGA)

Thermo gravimetric analysis (TGA) is performed on the handsheet sample. The equipment used is STA 409PC Luxx TGA, with Bruker Tensor 27 IR. The sample analyzed was less than 100 mg. The temperature profile for the experiment starts at 20 ^oC, then it is raised to 105 ^oC at a rate of 20 ^oC/min; it was held at 105 ^oC for 20 minutes. Thereafter, the temperature was raised to 500 ^oC at 20 ^oC/min, and then held at 500 ^oC for 20 minutes.

Air and nitrogen acted as purge and protective gas respectively. The flow rate of each gas was 30 mL/min.

Based on the fact that cellulose fiber and ink decompose at different temperatures, the amount of ink on the surface and interstitial portion of the fiber network can be estimated. Handsheet with varying degree of ink would have different percentage mass loss. Before, analysis, the samples were all preconditioned is same environment. Typically, the mass loss seen as the sample is heated from temperature to 105^oC is mostly due to change in the moisture content of the sample. The moisture content of paper can be as much as 7%.

Nesbit used a TGA method to quantify ink content in fiber. Nesbit showed that a sample of 100% newsprint fiber starts decomposing at 285^{o}C and completely reduce to ash at 500^{o}C. Nesbit showed that the percent change in mass for newsprint from 100^{o}C to 500^{o}C is 99.3%. While for a 100% carbon black particles, the percent mass loss is only about 1% at 500^{o}C. Only the newsprint fiber would decompose in the temperature range 100^{o}C to 500^{o}C[17]. The carbon black is the major solid component of inks, typically about 70%. Binders make the reminder. The samples analyzed in this study would likely contain mostly fiber, inks and a small amount of fillers.

The underlining assumption is that the relative amount of the fillers, or any other component besides fiber, fines and ink, stays the same before (feed) and after (accept) flotation. However, the mass fraction amount of ink and fiber would be different for accept and feed.

4.5 Solid loss determination and deinking selectivity

The solid loss in a flotation process is determined from the ash balance of the feed, accept and reject.[18]

$$Yield_{Total} = \frac{Q_{Accept}}{Q_{In}}$$

$$Yield_{Fiber} = \frac{X_{FiberAccept} Q_{Accept}}{X_{FiberIn} Q_{In}}$$

$$Q_{In} = Q_{Accept} + Q_{\mathrm{Re}\,ject}$$

$$X_{FiberIn} Q_{In} = X_{FiberAccept} Q_{Acceot} - X_{Fiber\,\mathrm{Re}\,ject} Q_{\mathrm{Re}\,ject}$$

$$SolidsLoss_{Total} = 1 - \frac{X_{\mathrm{Re}\,ject} - X_{In}}{X_{\mathrm{Re}\,ject} - X_{Accept}}$$

Zhu et al. define a deinking selectivity concept that takes into consideration both ink removal and fiber yield loss in a deinking process[19]. The deinking selectivity is referred to as Z–weighted factor and it is defined below in equation (I):

$$RE_{ZE}=Z_E * RE \quad (I)$$

Where RE_{ZE} is Z- factor weighted ERIC reduction, RE is ordinary ERIC reduction, and Z_E is the ratio of percentage of ERIC reduction and percentage of fiber rejection loss or percentage of total solid loss. In this study, both percent total solid loss and percent of fiber rejection loss were used.

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CHAPTER 5 : BATCH SETUP

5.1 Summary

Batch flotation deinking was performed on recycled stock that contains flexographic ink newsprint in various amounts. Flotation deinking treatment alone was compared with a flotation deinking treatment that incorporates electric field technology.

For both the recycled stock that contains 20% and 40% flexographic ink newsprint, the treatment pulp samples or accepts shows ERIC reduction and increment in brightness for both kinds of treatment. But higher ERIC reduction and better brightness gain was observed for the treatment that incorporates electric field technology.

The amount of ash removed by the electric field treatment is higher that the treatment without it.

The objective of the set of experiments in the batch setup for flotation is to show impact of incorporating electric field. The degree of mixing and air injections mechanism was not optimized.

5.2 Introduction

Recycled newsprint paper provides a cheap source of raw material for the paper industry. The recycling of newsprint paper involves the separation of ink from the newsprint fiber. Removal of ink from fiber is done by flotation. Flotation deinking involves the removal of ink by air bubbles from fiber, ink and water dispersion.

Hydrophobic air bubbles easily remove oil-based inks during flotation. However, certain inks like hydrophilic flexographic inks are difficult to remove because they are very small and easily dispersed in water in conventional flotation treatment conditions.

When using the flotation process, ink particle should be greater than 50 microns in diameter to be effectively collected by air bubbles in the flotation cell[1]. Flexographic ink particles are smaller than 5 microns[2].

The deinking efficiency can be improved by introducing an electric field to the conventional flotation process especially for stock that contains flexographic ink. The convention flotation process occurs in a flotation cell and when the electric field is introduced, it also functions as an electrolytic cell. The electric field generates fine bubbles due to the electrolysis of water. The fine bubbles, which have high surface area, are able to interact well with the fine ink particles.[3]

5.3 Experimental Section

Conditions of flotation deinking that incorporates electric field technology

The electric field assisted deinking setup consists of a power source (with positive and negative terminal), and the flotation cell. The positive terminal is connected to the shaft of the stirrer while the negative terminal is connected the cell wall. The electric volts and current used can be varied. The electric volts and current could be adjusted by changes in conductivity or in the surface area of rod exposed to the pulp stock. With the flotation deinking that incorporates electric field; the flotation conditions are the same as the one without electric field except that the electric field is started when the air bubble is introduced (see Figure 4.2 described in section 4.1.2 batch setup).

Case A and Case B.

The chemicals used were Floatsan 209 [non-ionic surfactant; BASF]. 1 ml Floatsan 209 was diluted to 40 ml with distilled water and DowFAX 3B2 [anionic, alkyldiphenyl oxide Disulfonate surfactant; DOW]. 1 ml of DowFAX 3B2 was diluted to 40ml with distilled water respectively. The furnish that offset-ONP and OMG and furnish that flexo and offset-ONP and OMG were used in case A and case B respectively. The deinking chemicals and conditions are summarized in Table 5.1

Table 5-1Deinking chemicals and conditions

	Case A	**Case B**
Surfactant	**Floatsan 209**	**DowFAX 3B2**
Furnish	**Offset –ONP (75%)** **/OMG (25%)**	**Flexo-ONP/offset-ONP** **/OMG (20%)**
Chemicals	**1% Sodium silicate** **1% Sodium Hydroxide** **0.25% Floatsan 209**	**0.42 % Sodium silicate** **0.42% Sodium Hydroxide** **0.375% DowFAX 3B2**
Voltage during float	**0.04KV, 493milliAmp**	**0.02KV, 368milliAmp**
Pulping conditions	**9.1% consistency, 50^{o}C**	**11.1% consistency, 55^{o}C**

Pulping. All of the pulping experiments were conducted using a kitchen kid mixer (planetary mixer). Oil based-ONP of *Atlanta Journal and Constitution (AJC), and* Flexo-ONP of *Macon telegraphy (MT), and OMG* (school of chemical engineering newsletter) were used in this study. The mixture of AJC and OMG or AJC, MT, and OMG was soaked 8hrs before pulping. The chemicals were added at beginning of the pulping process.

Flotation. The flotation cell consists of a cylindrical container. All flotation deinking experiments were conducted using this cell. The cell has a capacity of 4.0 L. Its diameter is 17.2 cm. The volume of ONP/OMG pulp treated was 3000 ml. Conditions for flotation in the cylinder container are as follows: for case 1, pulp consistency, 1%, float time is 50 minutes; temperature 35^{o}C; air flow rate, 450 ml/min. and for case 2 the pulp consistency, 1%, 40 minutes; temperature 35 ^{o}C; average air flow rate, 316 ml/min. The volume of ONP/OMG pulp mixture treated was 3000 ml.

Handsheets are made from both feed (pulp samples before flotation) and accept (after flotation) pulps samples and analyzed for ERIC and brightness. Brightness and ERIC was analyzed by Technidyne Color touch 2 Model ISO. During handsheets preparation more ink particles tend to settle at the bottom of the handsheets, therefore ERIC and brightness values of the bottom of the handsheets tend to be different from those of the top. ERIC and brightness data for both the bottom and the top of handsheets was reported.

5.4 Results and discussion

5.4.1 Furnish containing offset–ONP furnish (Case A)

Table 5-2 ERIC, Brightness and their standard deviation of feeds and accepts of flotation deinking with the incorporation of electric field technology

	ERIC		*Brightness*	
	Feed (Std.)	Accept (Std.)	Feed (Std.)	Accept (Std.)
E.F.	1298(32)	618(26)	423(0.5)	48.1(0.3)
no E.F.	1298(32)	690(31)	42.3(0.5)	47.5(0.2)

ERIC

Two identical set of deinking experiments were repeated for the treatment that incorporated an E.F. and the treatment without E.F, for a total of four experiments. One 300 ml pulp samples collected before flotation (only one feed handsheet was made since all the feed is essentially same for all experiments) and two 300 ml pulp samples after flotation were used to make handsheet for each experiment (two pulp samples ensures the reproducibility of the handsheet formation procedure). The handsheets were analyzed for ERIC and Brightness (as discussed in section 4.2, multiple readings was collected across the entire surface of the handsheets both top and bottom)

For the treatment with electric field the average ERIC of the handsheets before flotation (feed) was 1300 and the ERIC of handsheets of pulp samples collected after flotation

(accepts) was 617. (See Table 5.2) The reduced ERIC of the handsheet of pulp sample collected after flotation represents the ink removed during flotation. There is a 48% reduction in ERIC. For the flotation in which electric field was incorporated the reduction in ERIC was 53%. Statistical analysis on ERIC data obtained from both treatments was performed. The P value was <0.01, i.e. the probability of the difference observed between both treatments occurring by chance is exceeding low.

Brightness

Both handsheets made from pulp samples collected before and after flotation were measured for brightness. The ISO brightness of handsheet sample collected after flotation (accepts) was higher than the brightness of handsheet sample collected after flotation. For the flotation without electric field, the brightness increment from before flotation to after flotation was 5.28 points (See Table 5.2). For the flotation with electric field the increase brightness increase was 5.84 points. Statistical analysis performed on the brightness data obtained from both treatments. The P value was <0.001, i.e. the probability of the difference observed between both treatments occurring by chance is exceeding low.

The yield loss both runs with electric field was 2.53%. Without electric field, the yield loss was 1.72%. (The yield losses was calculated as the ratio of reject to feed) The higher yield loss demonstrates more ink dirt is removed when electric field technology is incorporated into deinking. (A Z-weighted factor, a parameter that normalized the ERIC reduction with the yield loss, is discussed in Chapter 6 and appendix B)

Makris et al reported applying electric field to a mixed furnish of offset ONP and OMG[4]. The electrode assembly or sparker was submerged in flotation cell and the unit

was discharged once every 3 seconds for 5 min or10min at 3 KV. The sparking was introduced in two forms, before and during flotation. Improvement in brightness is observed when sparking was applied before flotation but no improvement was seen when sparking was applied during flotation.

The sparking was applied to suspension of toner ink and a flexographic ink decreases the pH and zeta potential of the suspension, suggesting that the particles are oxidized. The increased negative charge on the ink/toner particles should inhibit redeposition on the negatively charged fiber. The furnish treated however, did not contain either flexographic or toner ink

Makris et al suggested that sparking during flotation does not improve the brightness because sparking introduces shock wave, which distorts the bubble size distribution. The flotation efficiency is optimal when the bubble size and particle-size distributions overlap[5]. The changes in the bubble size distribution adversely affect the overlap between the bubbles and particle size.

In this current study, electric field applied during flotation improves flotation efficiency. In this procedure is voltage applied is about 40V and also the voltage was continuously applied. As mentioned in section 3.1 electric field generates fine bubbles by electrolysis of water. These bubbles size are much smaller than bubbles generated by the introduction of air through air stones (***dispersed air***).

The electric field may also improve deinking of recycled stock containing flexographic ink. These fine bubbles are not too larger than the flexographic ink particle,[6,7] as a result, improved ink removal and increased brightness gain is expected.

The bubble size generated by electric field give a better overlap with flexographic ink size. The following discussion is on treating flexographic ink ONP with electric field

5.4.2 Furnish containing flexographic–ONP furnish (Case B)

The presence of flexographic ink newsprint in recycled stock causes severe problems for conventional flotation deinking mill. The problems include extreme darkening effect on the stock, ink fragmentation, ink redeposition and water contamination. Three different stock mixtures each containing different amount of flexographic ink newsprint was used to demonstrate the impact of flexographic ink on recycled stock (see Table 5.3).

The 0% flexo mixture refers to the pulp sample that contains 0% flexographic ink newsprint, 70% AJC and 30% OMG. 20% flexo refers to the pulp sample that contains 20% flexographic ink newsprint, 60% AJC and 20% OMG. While 40% flexo refers to pulp samples that contain 40% flexographic ink newsprint, 40% AJC and 20% OMG. The ERIC of the feed stock mixtures increases as the amount of flexographic ink newsprint increases in the recycled stock. Higher ERIC value is largely due to dispersed flexographic ink contained in flexo-ONP, the finely disperse flexographic inks have a higher surface area and its light absorption characteristic nearly maximized.

Table 5-3 Effect of flexographic ink newsprint in recycled stock on ERIC

	0% Flexo-ONP	*20% Flexo-ONP*	*40% Flexo-ONP*
ERIC (Std.)	1298(31)	1945(177)	3088(400)

ERIC Measurement

Table 5-4 ERIC and Brightness for feed and Accept. Accept standard deviation.

			Feed ERIC	ERIC Accept (Std.)	% Reduction in ERIC	BRIGHTNESS (ISO %) Feed	BRIGHTNESS (ISO %) Accept (Std.)	% BRIGHTNESS GAIN
BOTTOM	20% FLEXO	E.F.	2097	1192 (16)	43	34.5	40.4 (0.1)	17.1
		no E.F.	2097	1988 (85)	5	34.5	34.6 (0.2)	0.3
	40% FLEXO	E.F.	3443	2280 (94)	34	26.6	31.2 (0.6)	17.3
		no E.F.	3443	3146 (42)	9	26.6	27.2 (0.1)	2.3
TOP	20% FLEXO	E.F.	1790	928 (25)	48	36.9	43.6 (0.3)	18.2
		no E.F.	1790	1063 (17)	41	36.9	42.4 (0.1)	14.9
	40% FLEXO	E.F.	2733	1631 (48)	40	30.3	36.1 (0.3)	19.1
		no E.F.	2733	1876 (83)	31	30.3	34.5 (0.4)	13.9
AVERAGE TOP & BOTTOM	20% FLEXO	E.F.	1943	1060 (153)	45	35.7	41.9 (1.9)	17.4
		no E.F.	1943	1526 (536)	21	35.7	38.5 (4.5)	7.8
	40% FLEXO	E.F.	3088	1956 (379)	37	28.5	33.7 (2.9)	18.2
		no E.F.	3088	2511 (735)	19	28.5	30.6 (4.2)	7.4

The feed and accept ERIC is higher for the pulp sample that contains 40% flexographic ink newsprint when compared to the pulp sample that contain 20% flexographic ink newsprint. In other words there more ink in the pulp samples containing 40% flexographic ink newsprint. When the pulp samples are treated with flotation deinking, there is reduction in

ERIC values whether or not electric field technology is incorporated into the treatment. Table 5.4)

For 20% flexo, the top of the accept handsheet shows a 40% reduction in ERIC for the flotation deinking without electric field. While in the treatment that incorporates electric field there is a 48% reduction in ERIC. However, analysis of the bottom of the handsheet clearly highlights the impact of electric field technology. The bottom of the handsheet shows ERIC reduction of 43% for treatment with electric field, while without electric field, the ERIC reduction is only 5%. At 40% flexo, the bottom of the handsheets shows an ERIC reduction of 37% for treatment with electric field, while without electric field the ERIC reduction is only 9%. The ERIC of the top and bottom show two- sidedness. During the sheet formation (see section 4.2 for handsheet preparation), fiber collects on top of the filter paper to form pad, while the water drains. In the meantime, ink settles to the bottom of the pad. As a result, the ink is unevenly distributed between the top and bottom of the pad or handsheet causing two-sidedness. To reduce two-sidedness, alum could be added to sequester the ink on the fiber during handsheets preparation (in chapter 6, handsheet for analysis were made with alum).

Brightness measurement

The feed and accept brightness is lower for the pulp sample that contains 40% flexographic ink newsprint when compared to the pulp sample that contain 20% flexographic ink newsprint. In other words there more ink in the pulp samples containing 40% flexographic ink newsprint. Brightness is typically inversely proportional to ERIC.

For 20% flexo, the top of the accept handsheet show a 15% increase in brightness for the flotation deinking without electric field. While in the treatment that incorporates electric field

there is an 18% increment in brightness. Again, analysis of the bottom of the handsheet highlights the impact of electric field technology. The bottom of the handsheet shows a brightness increase 17% for treatment with electric field, while without electric field, the brightness increase is only 0.3%. (See Table 5.4)

At 40% flexo, the bottom of the handsheets shows a brightness increment of 17% for treatment with electric field, while without electric field the brightness increment is only 2%.

In the batch setup, the entire stock is exposed to the electric field for the entire duration of flotation. Moreover, in the batch setup, there is a slight increment in pulp slurry temperature due to heat dissipation from the electrode into the slurry. In chapter 6, only a fraction of the stock is exposed the electric field at a given time and also a temperature control mechanism was implemented in the semi-continuous setup.

The batch setup experiments are reproducible as shown in section 5.4.1, for the furnish containing offset-ONP. For the set of experiments with the furnish containing flexographic–ONP, the experiments were not repeated. However, there is a general consistent trend observed; the electric field assisted flotation seems to improve deinking efficiency.

The batch setup made up of small volume bucket. A lab stirrer provides the mixing energy and air is pump through air stones. Also the entire stock is exposed to the electric field during flotation. The rejects were scoop out manually.

Industrial scale flotation tank would be much more complete with different mixing and flotation zone within the tank, specially designed rejects collection mechanism, and special air injections system. In chapter 6, a more widely accepted industrial bench scale laboratory flotation cell is used for the study

5.5 Conclusion

A non-ionic surfactant and an anionic surfactant were used in the deinking process. It is shown that by the combined action of surfactant, and fine hydrogen and oxygen bubbles, flexographic ink can be removed from recycled stock.

For the furnish containing offset ONP, the ISO brightness of the handsheets is 11% higher and the ERIC reduction is 5% greater when an electric field is incorporated into flotation deinking.

For the furnish containing 20% flexographic ONP, The bottom of the handsheet shows ERIC reduction of 43% for treatment with electric field, while without electric field, the ERIC reduction is only 5%. At 40% flexo ONP in the furnish, the bottom of the handsheets shows an ERIC reduction of 37% for treatment with electric field, while without electric field the ERIC reduction is only 9%.

Surfactants mainly help to detach the ink from fiber and to improve frothing, though the wettability of the ink is not quantify, it could be suggested that surfactant impacts hydrophobic properties on the ink particles.

Bubbles, which are generated by electrolysis, provide extremely high surface area to which flexographic ink particles can attach. Moreover, there was a slight gain in temperature with electric field, which may play a secondary role in improving the deinking efficiency. For furnish containing offset ONP, the yield loss is about for about 50% greater with electric field, thus more ink dirt was removed in the froth during deinking with electric field compared to deinking without electric field.

Higher ERIC reduction and better brightness gain was observed for the treatment that incorporates electric field technology.

5.6 References

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CHAPTER 6 : SEMI-CONTINOUS SYSTEM

6.1 Summary

A semi-continuous flotation cell, which incorporates an electrolytic cell, was used to collect inks from newsprint pulp slurry.

The impact of pulping time and temperature on deinking of 100% flexographic newsprint (flexo-ONP) was investigated, using an electric field-assisted flotation. Longer pulping time reduced the deinking efficiency-measured by the percent reduction in effective residual ink concentration (ERIC)-by 5%. While higher temperature improved deinking efficiency by 3%. For longer pulping time, the use of electric field improved deinking efficiency by as much as 5%. For higher temperature, the use of electric field further improved deinking efficiency by 2%.

The impact of alkali charge, percent solid (consistency) during flotation, surfactant and soap concentration of furnish mixture- 48% flexo-ONP, 30% offset-ONP and 22% Old magazine (OMG) - was studied using the electric field-assisted flotation. Unlike 100% flexo-ONP, this furnish contains both flexographic and offset inks, which have different ink size and chemistry. On average, considering the variables, the use of electric field improved deinking efficiency by 3%. The best deinking efficiency was achieved at 1% consistency, when sodium hydroxide, and surfactant and soap are added, combined with electric field. The deinking efficiency was corroborated with Thermogravimetric analysis.

Deinking selectivity of the electric field-assisted flotation was discussed using a Z-weighted factor parameter. Finally, a mechanism for improved deinking efficiency with electric field is inferred based on ERIC, reject volume and total reject data.

6.2 Introduction

The motivation behind the use of water-based flexographic ink is the reduction of the emission of volatile organic carbon compounds associated with many conventional solvent-based types of ink. The printing quality of water-based inks is crisp and the print has a lower rub off and see-through.[1] [2]

A wastepaper furnish which contains flexographic printed ONP is difficult to deink by conventional flotation process. The problem with flexographic inks is related to its composition and properties. Flexographic inks are made of hydrophilic pigment particles, which are difficult to deink, by air bubble flotation. Flexographic ink particle diameter is 0.3-1μm, and offset ink particle diameter is 2-30 μm[3]. McCool describes the removal efficiency of contaminants as a function of their particle size, and showed that flotation deinking is more effective in removing particles larger than 10 μm[4].

Flexographic inks consist of carbon black pigments and acrylic resin binders that disperse the pigments in water. The poor floatability of water-based inks can be ascribed to the water-based acrylic resin, which in an alkaline medium prevents ink agglomeration by electrostatic and steric repulsion mechanisms[5] [6]. These small hydrophilic inks are ideal for deinking by washing. Washing can effectively remove ink particles, which are less than 10 μm in diameter and involve a series of diluting and de-watering (thickening) processes[7]. However, washing consumes a large amount of water, and an elaborate water decontamination process is needed to clean the wastewater. Also, the yield loss associated

with washing is economically unacceptable. A single wash deinking stage can have up to 35% yield loss[8].

Neutralization of the dispersion power of the acrylic resin by in non-alkaline condition during deinking has proved to be partially successful. Based on the fact that flexographic inks are not heavily dispersed in an acidic medium, Galland and Vernac[9] used a two-stage flotation process for deinking of wastepaper that contains flexographic printed material and offset printed-paper[10]. The first stage or loop removes the flexographic ink particles in a neutral condition. The second loop uses an alkaline medium to remove the conventional ink particles. Using 100% flexo newsprint, with a starting 35% ISO brightness, the first stage acidic flotation gave a final brightness of 40%. After thickening and bleaching, a second stage of alkaline flotation improved the brightness from 46% to 55% ISO brightness. An alkaline flotation only process for 100% flexo newsprint, improved the ISO brightness from 26% to 28%. At 26% ISO brightness, ERIC was 4760 ppm. Typical gains of pulp brightness around 10% ISO brightness[11]and ERIC reduction of 65% through flotation are common in laboratory or mill operations for conventional offset-ONP.

A separate study with 100% flexo newsprint, only 10% reduction in ERIC was attained in conventional alkaline deinking[12]. A new electric technology is proposed to improve deinking even in alkaline conditions.

6.2.1 A new electric technology for deinking flexographic ink

The electric field technology is essentially an electrolytic cell that consists of stainless steel electrodes and electrolyte solution. The electrodes are connected to an external power

source that drives non-spontaneous chemical reactions. In an electrochemical cell, the anode is still the location of oxidation, and at the cathode the reduction[13].

Electrolysis of water is the decomposition of water (H_20) into oxygen (O_2) and hydrogen gas (H_2) due to an electric current being passed through the water.

Care must be taken in choosing electrolyte, since an anion from the electrolyte is in competition with the hydroxide ions to give up an electrode. An electrolyte anion with less standard electrode potential than hydroxide will be oxidized instead of the hydroxide and no oxygen gas will be produced. At the cathode, a cation with a greater standard electrode potential than a hydrogen ion will be reduced instead and no hydrogen gas will be produce.

Typical chemicals used in deinking include, H_2O_2, NaOH, Na_2SiO_3, and $CaCl_2$. Ca^{2+} and Na^+ both have a lesser standard electrode potential than a hydrogen ion. However H_2O_2 has a greater standard electrode potential than hydrogen ion and will be reduced, until it is consumed. At the anode, SiO_3^{2-} is less than the standard electrode potential of hydroxide and is oxidize, until it is consumed. The Cl^- is not less than the standard electrode potential of hydroxide ions but will be oxidize if there is over-potential.

The premise for using an electric field in de-inking water-based inks is based on the fact that a process called electro-flotation has been employed in the removal of suspended particles from effluents. These suspended particles are normally less than 20 μm and have close to neutral buoyancy. Empirically, very small bubbles, often less than 100 μm in diameter, can be used for the removal of fine particles. One of the methods to accomplish this aim is electro-flotation in which bubbles are generated by electrolysis[14]. The removal of fine (<13μm) particle is high using bubbles of the order of 50 μm in diameter and do not require surface hydrophobicity.[15]

Moreover, the polyacrylic acid binder of the flexographic can ink react with the metal ions released from the anode electrodes in a process called electro-coagulation, if the electrode was aluminum[16].

While the effect of sodium hydroxide (alkali charge), surfactant and soap, pulping time, float temperature, and float consistency variables have been investigated separately in prior work, in this study, their effects were reconfirmed. The electric field technology could be combined with alkaline or neutral deinking chemistry, or surfactant to further improve deinking efficiency. The deinking efficiency is reported in terms of optical properties, ERIC and brightness. Finally, a mechanism was proposed for an electric field assisted deinking.

6.2.2 Effect of sodium hydroxide, surfactant and pulping time, temperature and consistency

Pulping time had an adverse effect on deinking efficiency and exacerbates ink fragmentation and re-deposition phenomena.[17]

The positive effect of temperature has been reported in flotation deinking. The higher temperature decreases surfactant surface tension of the aqueous suspension. The nonionic surfactants tend to have maximum surface activity near to the cloud point; in mostly case the cloud point occurs at higher than room temperature. Lower surface tension will cause reduced bubble coalesce and favor bubble break up and smaller bubble size[18]. It has been reported that smaller bubble size improve deinking efficiency[19]. Since the bubble size is smaller, the number of the bubble will be high. The higher the number of bubbles, the higher probability of collision between bubble and inks, and that may translate into improved deinking efficiency. Goto et al. attributed improved deinking efficiency to reduced surface tension[20].

The effective concentration of surfactant would be lower at lower percent solid of a suspension than at a higher percent solid suspension. The higher percent solid of suspension consequently higher surfactant concentration would improve impact on deinking efficiency.

In addition, the effect of sodium hydroxide on ink fragmentation has been reported. Ruzinsky et al. reported that the rate of ink detachment is increased when pulping chemicals, such as caustic, are used.[21] Ink detachment and fragmentation has an impact on the subsequent flotation process. Once the inks are successfully detached, they are more likely to be removed during flotation. However excessive ink fragmentation seen in flexographic ink can adversely affect flotation efficiency.

The furnish and ink type has an impact of deinking efficiency. Two kinds of furnish was used in this study, a 100% flexo-ONP (printed with flexographic ink) and a mixture of offset-ONP (printed with oil based) and flexo-ONP and Old Magazine (OMG). Galland et al showed that in the Centre Technique du Papier (CTP) two pH procedure, alkaline deinking is necessary for deinking offset ONP portion of the furnish mixture while, the acidic condition was suitable for flexo-ONP[10].

6.3 Equipment and Procedure

50 grams of furnish is pulped at 12% solid percent concentration (or consistency), and diluted to 4.4 L. The 4.4 L suspension is poured into the float cell (described in section 4.1.1), and then the circulating pump is turned on along with the airflow. The electric field is then turned on when it is needed. The froth formed during flotation is rejected through the overflow pipe and collected in the reject pan. The raw materials, the pulping chemistry and conditions, and float conditions are outlined in Table 6.1

Table 6-1 Raw Materials, Pulping and flotation conditions

	Raw Material (Furnish)	Pulping chemistry Tap water, 50°C; Water Hardness as $CaCO_3$, 40 ppm when 1 ml $CaCl_2$ is added or 120 ppm when 4 ml $CaCl_2$ is added.	Flotation conditions
Case 1	50 grams 100% flexo-ONP (*Macon Telegraph*)	NaOH 0.0% Sodium Silicate 0.0% Nonionic surfactant (Eka RF 4283) 0.06% Anionic surfactant (Eka RF 4031, Soap) 0.0% $CaCl_2$ 3 mL & H_20_2 4 mL Pulping consistency: 12% in Kitchen aid mixer Pulping Duration: range from 5 to 20 minutes	Airflow rate: 10 ft^3/hr Float time: 20 minutes Float volume 4.4 L
Case 2	50 grams 48% flexo-ONP 30% offset-ONP (*AJC*) 22% OMG (*Young Money Magazine and CHBE Newsletter 2005*)	NaOH 0.0% or 0.9% Sodium Silicate 0.0% Nonionic surfactant (Eka RF 4283) 0% or 0.02% Anionic surfactant (Eka RF 4031, Soap) 0% or 0.06% $CaCl_2$ 4mL & H_20_2 1mL Pulping consistency: 12% in Kitchen aid mixer Pulping Duration: 7 minutes	Airflow rate 4 ft^3/hr Float time: 12 minutes Float consistency: 0.5% to 1%. Float temperature: 20 °C or 45°C. Float volume 4.4 L

Table 6-2 Reproducibility study, raw materials and deinking conditions

Raw Material (Furnish)	Trial 1	Trial 2
48% flexo-ONP, 30% oil-based ONP (*AJC*) 22% OMG (*Young Money Magazine and CHBE Newsletter 2005*)	Float consistency at 1%, Nonionic surfactant used was EKA RF 4031 250 µl (0.5%) EKA RF 4283 10µl (0.02%) The float time was 10 minutes and electric field was 800 volts No alkaline charge (i.e. no sodium hydroxide)	Float consistency was 0.5%, and Float time was 12 minutes. Electric field of 1000 volts was used. No surfactant Alkaline charge 0.5% consistency.

Handsheet Analysis:

Handsheets were made from both feed (pulp samples before flotation) and accept (pulp slurry after flotation) pulp samples and analyzed for ERIC and brightness by a Technidyne Color touch 2 Model ISO. R. D. Haynes' procedure for making handsheets was followed and 1 ml of 12% alum was added to the pulp slurry prior to handsheet construction. The addition of alum ensure that all the inks is capture in the handsheet and not washed away during handsheet formation[22]

Experiment design:

To investigate multiple parameters of interest, for instance the effect of pulping time or float consistency on deinking efficiency, a 2^n factorial design of the experiment was employed. "n" represents the number of the parameters of interest and 2 represents the two levels; a high and a low level for each parameter. Each parameter is considered an independent variable and the measurable response to changes in each parameter is referred to as an observation.

From the observation, the Yates algorithm is used to compute the estimated effects of each parameter or a combination of parameters. The observation and estimated effects are typically reported in a table. The first row of the estimated effects column is the grand total effect; the remaining estimated effects represent how the parameter or combinations of parameters affected the observation. If the estimated effect for a parameter is negative and high in magnitude in comparison to the grand total effect, then that parameter(s) has an adverse and huge impact on the observation. The estimated effect is interpreted as how the high level of that parameter would affect the observation.

Reproducibility

The reproducibility of results using a semi-continuous flotation cell was determined using two separate trials. Table 6.2 outlined the conditions for the trials. In each trial, three identical runs were performed. The results of the three identical runs for each trial are summarized in Table 6.3. Now that the reproducibility, given by standard deviation is now calculated, different methods can be compared. When the same stocks undergoes two different treatments, if the difference of the accept ERIC values is greater than the standard deviation given by the reproducibility study, the difference is considered significant.

Table 6-3 ERIC values after repulping and after flotation, Standard Deviation Values (STD), and Coefficients of Variation (CV).

	ERIC (ppm)	Average	Std	(Std/average)*100, CV%
TRIAL 1				
Feed	2941	2964	56	1.91
	2923			
	3029			
Accept	2454	2440	16	0.65
	2446			
	2423			
TRIAL 2				
Feed	2719	2760	76	2.74
	2753			
	2807			
Accept	1792	1842	49	2.67
	1837			
	1896			

6.4 Results and discussions

6.4.1 Pulping time, float temperature and electric field

The float study was performed using materials and conditions discussed as Case 1 in Section 6.3 (see Table 6.1). A 2^3 factorial design of the experiment was used to investigate the effect of the following parameters on deinking efficiency; pulping time, float temperature and electric field. The two levels for the electric field, pulping time, and temperature were 0 & 1500 volts, 5 minutes & 30 minutes, and 30 ^oC & 43 ^oC respectively. The results are summarized in Table 6.4 and Figure 6.1. The deinking efficiency is reported in terms of percentage change (or reduction) of the pulp slurry's ERIC.

Both the electric field and float temperature have a positive estimated effects i.e. the treatment with an electric field and higher temperature have a positive effect on percentage change of ERIC in the pulp slurry (see Table 6.1). The estimated effects of pulping time is negative, which means it has an adverse effect on deinking efficiency and exacerbates ink fragmentation and re-deposition phenomena.[23] The accept ERIC is strongly dependent on the ERIC of the feed as shown in Figure 6.1.

At 1% the slurry exhibited a non-Newtonian behavior. The viscosity of the 1% consistency stock at 32^oC for the stock pulped for 5 minutes and 20 minutes were 4-8 cP and 3-8 cP respectively. The primary effect of pulping time remains to be on ink fragmentation and deposition. Longer pulping time reduced the deinking efficiency-measured by the percent reduction in ERIC-by 5% (compare experiment no. 1 and 5, see Table 6.4). While higher temperature improved deinking efficiency by 3% (compare experiment no. 1 and 3). For longer pulping time, the use of electric field improved deinking efficiency by as much as 5%

(compare experiment no. 5 and 6). For higher temperature, the use of electric field further improved deinking efficiency by 2% (compare experiment no. 3 and 4).

A paired "t test" was performed, for treatment with and without electric field, on the percentage change (reduction) in the pulp slurry's ERIC, using the data from Table 6.4. The two-tailed P value equals 0.0249; that is, the difference is considered to be statistically significant.

The positive effect of temperature may be related to its effects on surfactants surface tension. The temperature of the solution at which the solution becomes cloudy as the temperature is gradually increased is referred to as the cloud point. The nonionic surfactants tend to have maximum surface activity near to the cloud point temperature. The surfactant surface activity would be greater at 43^{o}C than at 25^{o}C. The cloud point of the nonionic surfactant, EKA 4283, is greater than 43^{o}C for a 1% aqueous solution. The temperature would also have an effect on the viscosity of the pulp slurry; higher temperature would reduce viscosity. Zahradnik et al reported increasing liquid viscosity promotes bubble coalescence because of drag forces[24]. This suggests that lower fluid viscosity would promote reduction of bubble coalescence[25]. The smaller bubble size would improve the deinking efficiency. [26] [27].

The adverse effect of pulping time on ink fragmentation and redeposition has been previously investigated[23]. However, even at longer pulping time, there is a slight improvement in deinking efficiency with an electric field. The improved deinking efficiency observed with introducing an electric field can be attributed to the fine bubbles, which are generated by the electrolysis of water.[28] [29]

Table 6-4 2^3 Factorial design of experiment. X1, X2, X3 represents electric field, Temp., Pulping time variables respectively.

Experiment No	Electric field (volts) X1	Temp (^oC) X2	Pulping time (min) X3	% Change of ERIC Observation	Estimated effects of variables	Variables
1	0	30	5	39.9	41.70	
2	1500	30	5	41.9	3.60	X1
3	0	43	5	42.9	2.48	X2
4	1500	43	5	45.1	-0.03	X1X2
5	0	30	20	34.8	-4.13	X3
6	1500	30	20	40.0	1.48	X1X3
7	0	43	20	36.8	-0.63	X2X3
8	1500	43	20	41.7	-0.13	X1X2X3

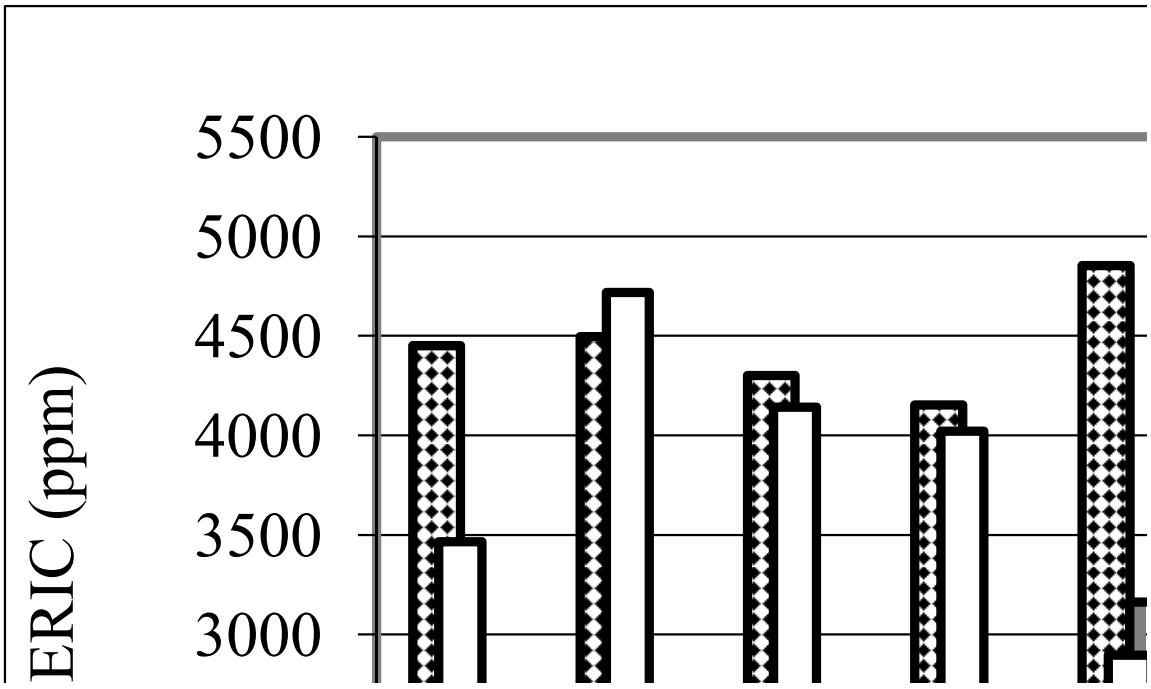

Figure 6-1 Feed and accept ERIC values and solids loss % as function of deinking parameters

6.4.2 The impact of alkali charge, flotation consistency, surfactant and soap and electric field on deinking efficiency

The effect of floatation consistency, feed pulp slurry pH, surfactant, and soap dosage on float deinking efficiency was investigated to get an optimized condition that works well with an electric field. These four independent variables were investigated using a 2^4 factorial design. In all, a total of 16 experiments were carried out (see Table 6.5). Since none of the experiment was repeated, the reproducibility of the flotation cell was determined. The furnish used for the reproducibility study is described in Table 6.2 (the furnish is similar to the one used in Case 2 in Table 6.1). The raw data are summarized in Table 6.6.

Table 6-5 2^4 design of experiment

Experimental #	*Electric field (volts)*	*NaOH (pH)*	*Consistency (%)*	*Surfactant (µL)*	*Soap (µL)*	*Feed (pH)*
9	0	0	0.5	0	0	8.08
10	1000	0	0.5	0	0	7.78
11	0	5	0.5	0	0	9.86
12	1000	5	0.5	0	0	9.83
4	0	0	1	0	0	7.56
8	1000	0	1	0	0	7.62
3	0	5	1	0	0	9.37
7	1000	5	1	0	0	9.76
13	0	0	0.5	10	30	8.00
14	1000	0	0.5	10	30	8.05
15	0	5	0.5	10	30	10.10
16	1000	5	0.5	10	30	10.13
1	0	0	1	10	30	7.98
6	1000	0	1	10	30	7.63
2	0	5	1	10	30	9.95
5	1000	5	1	10	30	10.11

Table 6-6 Raw Data; Accept ERIC and Percent change in ERIC

Sodium Hydroxide and Consistency	*Surfactant & Soap /no e.f.*		*No surfactants & Soap /no e.f.*		*Surfactant & Soap /(e.f.)*		*No Surfactant & soap /(e.f.)*	
	% Change in ERIC	Accept ERIC	***% Change in ERIC***	Accept ERIC	***% Change in ERIC***	Accept ERIC	***% Change in ERIC***	Accept ERIC
Exp. #	*13*		*9*		*14*		*10*	
No NaOH/0.5%	***22.9***	1767	***22.7***	1776	***24.7***	1734	***29.8***	1650
Exp. #	*15*		*11*		*16*		*12*	
NaOH /0.5%	***35.8***	1735	***19.9***	2205	***44.8***	1495	***19.0***	2169
Exp. #	*1*		*4*		*6*		*8*	
No NaOH/1%	***28.6***	1636	***31.6***	1637	***33.1***	1614	***40.4***	1401
Exp. #	*2*		*3*		*5*		*7*	
NaOH/1%	***46.1***	1422	***44.2***	1515	***49.1***	1333	***33.2***	1846

6.4.2.1 The effect of consistency, sodium hydroxide and surfactant on deinking efficiency

First, the effect of consistency, i.e. the percentage of total dry solids in the slurry, on deinking efficiency is examined. Considering all the other parameters, it is clear that the accept ERIC value at 1% consistency is lower than at 0.5%. (See Table 6.6)

Unlike at 1% consistency, foaming and frothing was sparingly observed at 0.5% consistency. When surfactant is added to an aqueous suspension, the surface tension of the suspension decreases as the surfactant concentration is increase, until the surfactant reaches a critical micelle concentration (CMC), were the surface tension remains same even above the CMC[30]. No measurement was done to determine the critical micelle concentration, in the

work, but one could argue that if the surfactants concentration were at least at CMC and above, then the surface tension would be same at 0.5% and 1% consistency. The apparent surface tension measurement was 56.9 (±0.8) dynes/cm and 54.6 (±0.1) dynes/cm at 0.5% and 1% consistency respectively. If the surface tensions were same, then frothing and foaming behavior would be at least similar. The frothing and foaming behavior at the two consistencies is consistent with the region where surface tension decreases with surfactant concentration increases. The dosage of soap is higher than nonionic surfactant. The CMC of nonionic surfactants is about two orders of magnitude lower than the corresponding anionic (or soap) with the same alkyl chain length.

The difference in viscosity of the pulp slurry at 1% (5-8.00cP) and 0.5% (0.4-2.00cP) consistencies may be significant enough to affect bubble size distribution in the flotation stage. But the efficiency was higher for the more viscous 1% solid consistency slurry than for 0.5%, which means the deinking efficiency, at least for this case, is dominated by surfactant concentration and surface tension effects. Further increase in pulp slurry consistency does not necessary improve deinking efficiency, because the slurry would become increasingly viscous as the fiber begins to form network. Heindel showed that at 1.5% consistency excessive coalescence of small bubbles occurs forming large ones.[31]

The "t test" performed on the percent ERIC reduction at 0.5% consistency and at 1% consistency yields a P value of 0.0054, which is statistically significant. (Compare exp. # 2, 3, 5, & 7 to exp. # 15, 11, 16, & 12 respectively in Table 6.6)

Next, the effect of sodium hydroxide and surfactant concentrations, on deinking efficiency was studied. For mixed furnish like flexo-ONP/offset-ONP/OMG, the effect of NaOH adversely affect ink fragmentation but improves fiber swelling and ink detachment

from fiber during pulping. Ink detachment and fragmentation has an impact on the subsequent flotation process. Once the inks are successfully detached, they are more likely to be removed during flotation.

The percent change in ERIC for the NaOH and surfactant combined has a markedly better deinking efficiency than when no NaOH is added and without surfactant (compare exp. #15 and exp. #9 respectively in Table 6.6). In contrast, higher accept ERIC, which is primary due to high feed ERIC, is seen when adding NaOH (adjusting to more alkaline pH) and in the absence of surfactant (compare exp. #15 and exp. #11). Though adding NaOH aggravates the feed ERIC, the combination of sodium hydroxide and surfactant has synergic effect since it gave the lowest accept ERIC. The surfactant does not show any distinguishing effect on accept ERIC with and without sodium hydroxide. Surfactant is only effective in the presence of NaOH. Electrolyte, like sodium hydroxide and calcium chloride can reduce or inhibit bubble coalescence[32].

6.4.2.2 Effect of electric field on deinking efficiency

The percent reduction in ERIC is higher with electric field except for the following pair; compare exp. # 3 & 11 without electric field to exp. # 7 & 12 with electric field respectively (See Table 6.6). A paired "t test" of the percent reduction in ERIC excluding experiments 3,7,11, and 12 yielded a P value of 0.0051, this is very statistically significant. Experiment 3, 7, 11 and 12 was performed without surfactants and with the additional of 0.09% sodium hydroxide. The average feed pH value was 9.8 when NaOH is added compared to 7.8 in the absence of NaOH. Under these conditions, pH 9.8, the flexographic inks are

highly solubilized and much dispersed- and the higher flotation efficiency without electric compared to electric field seen here may be an experimental anomaly and error.

Flotation at 1% consistency and the addition of surfactant with electric field gave the best deinking efficiency (exp. # 5 see Table 6.6). It is clear that the bubble stability affects deinking efficiency. The bubbles generated by electrolysis of water are about 30 μm in diameter[28]. The micro bubble promotes better bubble stability and has lower bubble coalescing. The size of bubbles from the venturi type injector is reported to be on the order of 1500 μm[33]. The size distribution of bubbles is broadened when the different bubble sources is combined. Large number of bubbles and bubbles of smaller size would results in more collision with ink particles; consequently there would be an increase in the amount of reject.

In general, the delta ERIC, the ERIC difference between feed and accept, with an electric field treatment is higher in comparison to the delta ERIC without an electric field. To be considered scientifically significant, however, the delta ERIC must be higher by a magnitude greater than the experimental noise- the standard deviation determined from the reproducibility experiments (Table 6.3)

SCANNING ELECTRON MICROSCOPE (SEM)

The accepts handsheet obtained from treatment without electric field and treatment with electric field (exp.# 15 and exp. #16 respectively in Table 6.6) were examined using scanning electron microscopy. The SEM images reveal that most of the external surfaces of the accepts from treatment without electric field are covered with ink; practically no cellulose fiber is seen (See Figure B.1 in Appendix B). In contrast, the accepts obtained from the electric field treatment show portions of the external surface not covered with ink, thus some strand of cellulose fiber is seen. (See Figure B.2). However, the SEM images taken are only a

miniature fraction of a micron of the handsheet total surface area, the results in not conclusive.

TGA

Based on the fact that cellulose fiber and ink decompose at different temperatures, the amount of ink on the surface and interstitial portion of the fiber network can be estimated. Samples of feed and accepts (listed as experiment 16 and 15 in Table 6.6) were analyzed using a Thermogravimetric Analysis (TGA) device. Before, analysis, the samples were all preconditioned is same environment. The starting temperature of the TGA analysis was 30^{o}C. At the 100^{o}C the percent change in mass of the samples was 4%, the change in mass is likely due to change in the moisture content of the sample as the device is heated from 30^{o}C to 100^{o}C (See Figure 4). The moisture content of paper can be as much as 7%.

Only the newsprint fiber would decompose under the temperature range 100^{o}C to 500^{o}C[34]. The carbon black is the major solid component of inks, typically about 70%. Binders make the reminder. The samples analyzed in this study would likely contain mostly fiber, inks and a small amount of fillers. The mass fraction amount of ink and fiber would be different for accept and feed. Clearly, the change of brightness and ERIC before and after flotation suggests there is a change in the amount of ink. From the TGA analysis, the percent change of the samples' mass from 100^{o}C to 500^{o}C is 82.3%, 84.9% and 87.5% respectively for the feed, for the accept without and with electric treatments (See Figure 4). At low temperatures up to 290^{o}C, the percent change of mass versus temperature profile is identical for the feed and both accepts. At temperatures greater than 290^{o}C, the accept from the electric field treatment begin to show a markedly different profile, this behavior is consistent with a sample that contains 100% cellulose fiber, since it has relatively more fiber and less inks than the other samples

(feed and accept without electric field). Moreover, at temperatures greater than 340^{o}C, the mass loss profile begins to be different for the sample of the feed and accept without electric field treatment. The samples' mass loss is a sum of the mass loss of the cellulose and the mass loss of the ink. But the mass fraction of cellulose and ink in each sample may be different. Since the mass loss of the ink fraction is negligible under the temperature range been considered, then if a sample has a higher ink mass fraction, the total mass loss of the sample would be less at given temperature. At a temperature greater than 350^{o}C, mass loss profile of the feed sample is distinguished from the sample accepts without electric field treatment because the feed sample has higher ink mass fraction and less fiber than the accept sample. At 500^{o}C, the feed had the least amount of percent mass loss from its original mass. The accept obtained from treatment with an electric field had a greater percent mass loss than the accept obtained from treatment without it. The average sample weight used for the TGA analysis was 50 mg. The difference in percent mass loss temperatures from 100^{o}C to 500^{o}C for the different samples is significant, considering the fact that the mass fraction of ink in 1% consistency suspension of newsprint pulp slurry is roughly 0.1% approximately 50μg[29]. An alternative process using high temperature furnace (using ash content data in Table B-6) also show similar mass loss as obtained with TGA analysis, for samples from experiments # 15 and # 16.

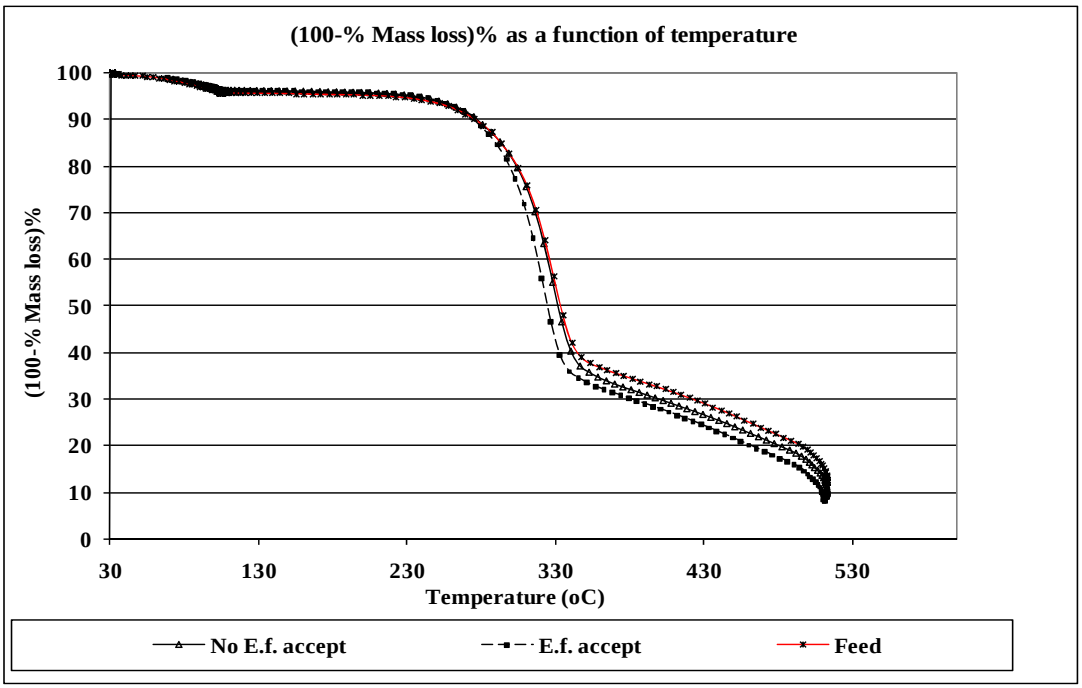

Figure 6-2 Mass loss profile of feed, accepts

6.4.3 Solid loss and deinking selectivity with electric field

The objective of the flotation process is to remove the detached inks from the fiber suspension by injecting air bubbles. The air bubbles collide and attach to the ink particles; the ink-bubble froth floats to the top and is rejected. Unfortunately, the bubble froth rejection process also rejects fibers, primarily as a result of the entrainment of fiber into the bubble network.[35] Fiber rejection loss is increased with an increase of froth rejection.[36] The increased ink removal and fiber yield are two contradictory requirements in flotation operations.

Pulp slurry prepared from 100% flexo-ONP (Macon Telegraph), with a pH of 6.75 and conductivity of 190 μS, was treated by flotation deinking. The flotation was done in the tank described in Figure 1, float time was 30 minutes and airflow rate was 3 ft^3/hr. The Z-weighted proposed by Zhu et al[37] was used to evaluate the overall selectivity performance of the deinking process that incorporated the use of an electric field. The results are summarized in

Table 6.7. At constant temperature and constant surfactant dosage, the Z-weighted factor (calculated either by using fiber loss or total solid loss) was higher when an electric field was used. Also, the solid loss was higher when an electric field was used. The raw data used to compute solid loss is shown in Table B.7. The average Z-weighted factor (based on total solid loss) is 18% higher with electric field compared to without electric field

Solid loss calculation gives possible clues to how an electric field helps to improve deinking efficiency, as observed in a lower ERIC of accept.

Table 6-7 Z-weighted factor.

Temperature (^oC)	*Electric field (K volts)*	*Surfactant put in concentration) (micro-liters) EKA RF 4031*	*ERIC (feed)*	*ERIC (Accept)*	*Solid loss*	*Z-weighted factor (% fiber loss)*	*Z-weighted factor (% total solid loss)*
25	0	0	3964	2797	5.7	6.76	5.9
25	1.25	0	3911	2282	8.6	9.06	7.9
48	0	10	3767	1946	9.4	10.57	9.3
48	1.25	10	3770	1621	11.8	11.85	10.3
25	0	30	3663	2347	12.9	3.966	3.6
25	1.25	30	3830	2284	15.6	4.42	4.0

6.4.4 Proposed mechanism of electric field assisted deinking

Table 6-8 Effect of electric volts on flotation deinking and rejects

Volts	*Accept ERIC value (Std)*	*Diff. b/w feed and accept ERIC value (ppm)*	*Reject Volume (mL)*	*Total Reject dry weight (Std)*
0	3397(7)	670	115	0.742 (0.045)
500	3071(202)	1248	122	0.744 (0.033)
1000	3218(13)	745	115	0.700 (0.025)

The amount of rejects (foams that contain air bubbles, water, ink, and fines) was measured as a function of time; the total volume is shown in Table 6.8. The voltage applied was varied from 0 to 1000 volts. The total reject dry weight is shown in Table 6.8. At 500 volts, the differences between feed ERIC and accept ERIC is greatest at 1248 ppm. Though the total reject dry weight and the reject volume for various electric field voltages is statistically similar, the accept ERIC values are different. A likely explanation is that the bubbles generated by electrolysis of water selectively collect the ink particles in the foam. The collection mechanism may be flotation or entrainment. The ink weight is only a fraction of the weight of a paper (about 0.1% of a 1% pulp slurry), but it greatly affects the optical property of the paper as seen in the ERIC values. The higher reduction of ERIC when an electric field is introduced during floatation suggests that the electric field treatment removes the dispersed fine ink particles that are responsible for higher ERIC. Small inks, of one micron or less, contribute more to the effective residual ink concentration[38]. The deinking efficiency does not show a linear response to electric field voltage (compare 500 volts to 1000 volts), one would expect higher voltage would drive more electrolysis of water, thus more fine bubble would be

formed. 1000 volts, is an overpotential considering able the electrochemical series potential range ± 4 volts. The overpotential may be driving other oxidation and reduction reactions besides electrolysis. Higher voltage may have had unintended adverse consequences on surfactant makeup and surface activity. Further study is needed to clarify the impact of varying electric field voltage intensity on deinking efficiency, what is clear however, is that electric field improved deinking efficiency compared to when it is not used.

6.5 Conclusion

The effect of the selected variables was investigated using a semi-continuous batch system in the presence of an electric field.

The effect of pulping time, temperature on flotation deinking in the presence of electric field was investigated using a 100% flexographic-ONP furnish. Increasing the pulping time from 5 to 20 minutes drastically reduced the percent reduction in effective residual ink concentration (ERIC) by 5% percent. The deinking efficiency is improved by 3% and 5% when the temperature from 25^{o}C to 43^{o}C and when an electric field is used respectively.

The effect surfactant concentration, solid percent or consistency and sodium hydroxide on flotation deinking in the presence of electric field using a furnish mixture, with different ink type (48% flexo-ONP, 38% offset-ONP, 22% OMG).

The float at 1% consistency was more efficient than at 0.5%, this improvement was attributed to lower surface tension. The apparent surface tension measurement was 56.85 (±0.8) dynes/cm and 54.6 (±0.1) dynes/cm at 0.5% and 1% consistency respectively.

Flotation deinking efficiency with and with electric field is compared; a paired “t test” of the percent reduction in ERIC excluding experiments numbers 3,7,11, and 12 yielded a P value of 0.0051, this is very statistically significant.

The deinking efficiency was reported as percentage change in ERIC (or percentage of ERIC reduction).

The deinking selectivity was reported as Z-weighted factor. A 100% flexo-ONP was used to perform this study at two temperature levels, and different surfactant levels in the presence of electric field .The average Z-weighted factor is 18% higher with electric field compared to no electric field.

The higher number and surface area of smaller size bubbles improved collision with fine inks and is a possible mechanism behind improved deinking efficiency observed when an electric field is used.

Thermogravimetric Analysis was used to corroborate the improved deinking efficiency observed and measured with ERIC.

A float study of deinking efficiency in terms of rejects volume and change of ERIC different was investigated at electric voltage levels of 0, 500, and 1000. The reject volume was same, but the reduction was different voltage level, showing that electric field selectively removes flexographic ink.

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CHAPTER 7 : WATER CLARIFICATION WITH ELECTRIC FIELD

7.1 Introduction

Deinking of flexo ONP by flotation is difficult. Because of the size (0.5μm) of the flexographic ink, deinking by washing is a better approach. However, the flexographic ink that ends up in the wastewater has to be treated. Washing also results in lower yield since some fiber fines ends up in the filtrate. Yield losses of up to 35% have been reported

A benefit of deinking by washing is that wastewater generated from deinking mills could be treated and reused. The well-known treatment methods include dissolved air flotation and sedimentation[1]. Dissolved air flotation (DAF) and sedimentation both require the use of a two polymer system. One chemical is used as flocculant and the other as a coagulant.

The two polymer system relies on 1) a coagulant polymer with a cationic charge and a low molecular weight to neutralize the anionic contaminants, and 2) a flocculant polymer with an anionic charge and a high molecular weight to create floc formation by a bridging mechanism.

DAF is used to purge flocculated ink and contaminants from process water for reuse in deinking mills. The objective of using DAF is to remove all the suspended solids with air bubbles. This objective is achieved by providing relatively quiescent conditions and small diameter air bubbles (about 0.01 to 0.1mm). These small bubbles are obtained by dissolving air at high pressures then releasing of the pressure.

For wastewater generated from plant deinking flexographic newsprint both ultra-filtration and membrane separation have also been used[2] [3]. The use of electrochemical cells to decontaminated water and waste water has been reported, however, a study of the uses of

electrochemical cells specifically for decontaminating waste generated from flexographic newsprint deinking as not been reported. Studies show that electrochemical cells are not always effective in COD reduction for all kinds of wastewater; the effectiveness is affected by the ionic content of the electrolyte solution [4]. Therefore, the use of electrochemical cells has to be examined for each water and wastewater source. Electrochemical treatment of ink can be found in the literature.[5] [6] But no study had been done that focuses on the various parameters of electrochemical cell on decontamination efficiency of flexographic ink wastewater. The parameters include the current density, treatment time, electrode type, and pH. The efficiency of the decontamination of the model and real flexographic ink wastewater by the electrochemical cell is reported in terms of cationic demand and turbidity.

7.2 Materials and Methods

Samples

Two type samples were treated; a wash deinking filtrate and a model flexographic ink dispersion.

Wash deinking filtrate

50 g of flexographic ink newsprint was pulped for 10 minutes at 12% solid consistency in a laboratory hydropulper. The pulped newsprint was diluted to 1% solid consistency. 2.5 L of the pulp slurry was screened using a 65 mesh screen. 1.78 L of the filtrate was collected and diluted to 10 L. Then 2 L of the diluted filtrate was treated in the electrochemical cell.

Model Flexographic ink

Water based ink is obtained from US ink. Typical ink composition is detailed in Table 7.1. [7] [8].

Table 7-1. Typical flexographic ink composition

Ink components	% Composition of flexographic ink.
Carbon black	16- 18
Styrene Acrylic Resin solutions	9-18
Polyethylene wax dispersion	2-4
Water	51-70

Electrochemical cell

Volume of the cell is 2500 mL; volume of sample treated is 2000 mL. Cathode: stainless steel with a surface area of 60 cm^2. Anode: aluminum or copper electrode with a surface area of 182 cm^2. At 400 mA, the anode current density is 21.9 A/m^2. The electrode material, electrode orientation, current density is a few factors that affect the electrochemical process. Excessive large current density would result in a significant decrease in current efficiency. Current density of 20-25 A/m^2 suffices for low maintenance operation[9].

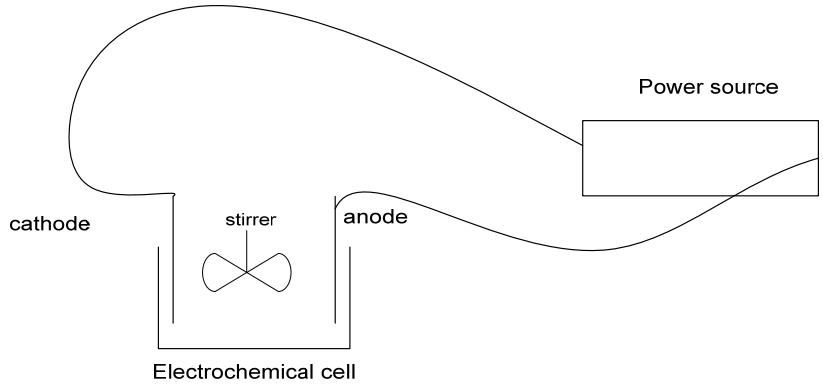

Figure 7-1 Schematic of an Electrochemical Cell

7.3 Experimentation

Sample was collected 0, 20, 40 minutes into treatment and analyzed for turbidity, cationic demand, conductivity and pH.

Turbidity

The samples collected at different treatment times are well mixed, and the initial turbidity measured. The collected samples are then allowed to stand unperturbed for 30minutes after which another turbidity or final turbidity measurement is taken. Turbidity is reported as Formazin Attenuation Units (FAU).

Cationic Demand

A Mutek PCD-03 particle charge detector was used to determine the cationic demand. The detector consists of a cell and a piston. The aqueous sample was placed in the measuring cell. Once the instrument is turned on, the piston of the cell oscillates and causes a high flow rate in the cell. Any charged materials or particles adsorbed to the cell wall will be separated from its counter ions by the flow and the movement of counter-ions creates a streaming current. Two electrodes in the cell pick up this current and display it on the unit. Most materials involved in papermaking have charged surfaces. Namely, fibers, fines, fillers, ink, and other papermaking additives carry a net negative charge. Some additives are cationic in nature and therefore, are attracted to the anionic components. The cationic particles, which are also known as or counter-ions, which are tightly bound to the surface of the anionic colloid, forms the Stern layer. The electrostatic forces at the stern layer are strong enough to prevent the displacement of the counter-ions by shear force. Outside of the stern layer is a grouping of loosely bound counter-ions known as the diffuse layer. The stern and diffuse layers make up the double layer. The ions in the diffuse layer are further apart and can be displaced when a

shear force is applied. The charge analyzer causes the shearing of counter-ions, and then measures the current generated by the movement of these cationic particles. The shearing of the counter-ions occurs between the Stern layer and diffuse layer, known as the slip-plane. The measurement of zeta potential is also based upon the double layer theory. The zeta potential is valid at the slip-plane. Essentially, the zeta potential is measured between the slip-plane and the bulk solution that is in ionic equilibrium. Whether the streaming current or zeta potential is being measured, adding an oppositely charged electrolyte or polyelectrolyte will cause the slip-plane to contract the particle surface. As the slip-plane contacts the surface, the streaming current or zeta potential will become less negative. Eventually, the isoelectric point will be reached, which is defined as a streaming current value equal to zero and where the solution is considered neutral (no net charge). If additional electrolyte is added, the system will become net cationic.

To determine the charge demand of a sample, a polyelectrolyte of the opposite charge is added until the isoelectric point is achieved. A polyelectrolyte is a standardized polymer with known charge density, also referred to as “titrant”. As explained previously, the slip plane contracts the colloidal surfaces, until there are no more counter-ions that are strongly bonded to each colloid. Thus, the Stern layer is nonexistent and the streaming current value goes to zero. The charge demand refers to the amount of titrant, in milliliters, that is required to bring a sample to the isoelectric point. Since the charge demand quantifies the number of charges in a volume of furnish, its value may be expressed in ml of titrant consumed by the sample to reach the isoelectric point. The polyelectrolyte’s charge density is known as “titrant normality” with units of equivalents/L. The charge demand (volume of titrant consumed) may be converted from milliliters (mL) to milliequivalents per liter (meq/L).

$$Charge\ Demand(meq/l) = \frac{Titrant\ Consumed(mL) * Titrant\ Normility(eq/L) * 1000(meq/eq)}{Sample\ Volume(mL)}$$

Converting the charge demand from mL to meq/L is especially useful if titrant with different normalities are used, or if different sample volumes are required. The titrant used was polyDADMAC @ 0.001 eq/L. The charge demand depends of the concentration of samples and degree of ionization of the colloid in the sample. If the titrant is cationic, the charge demand is sometimes called cationic demand.

7.4 Results

To evaluate the concentration of ink in the solution during treatment, a calibration curve of turbidity versus ink concentration was determined. As a function of pH and concentration, the turbidity increases with concentration of the ink. From the calibration curve (Figure 7.2), the ink concentration considered in this study is estimated.

The concentration of ink is also in direct relationship with cationic demand. Figure 7.3 shows that the cationic demand increases with increasing pH, but with constant pH, the cationic demand is higher for higher concentration of inks. The cationic demand of the inks at the two concentration levels is similar in acidic condition because the negatively charge inks are protonated. For the untreated sample (i.e. 0 minutes), each data point was collected twice, at 88 mg/L and 44 mg/L the average standard deviation were 0.0138 meq/L and 0.0219 meq/L respectively. However, for the treated samples (i.e. at 20 and 40 minutes) only one measurement was taken.

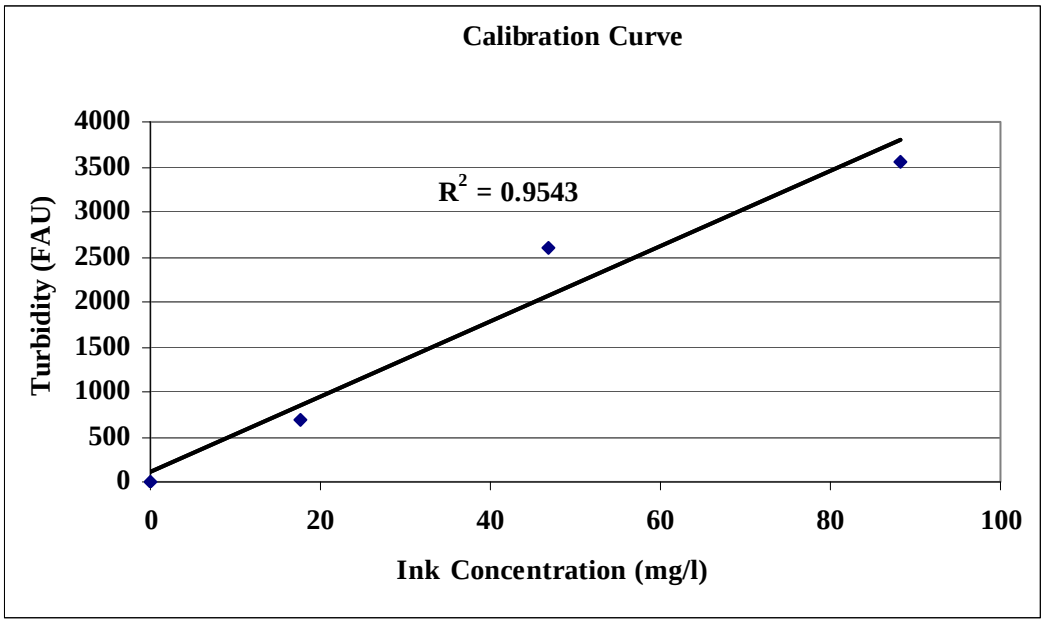

Figure 7-2 Ink Concentration Calibration Curve

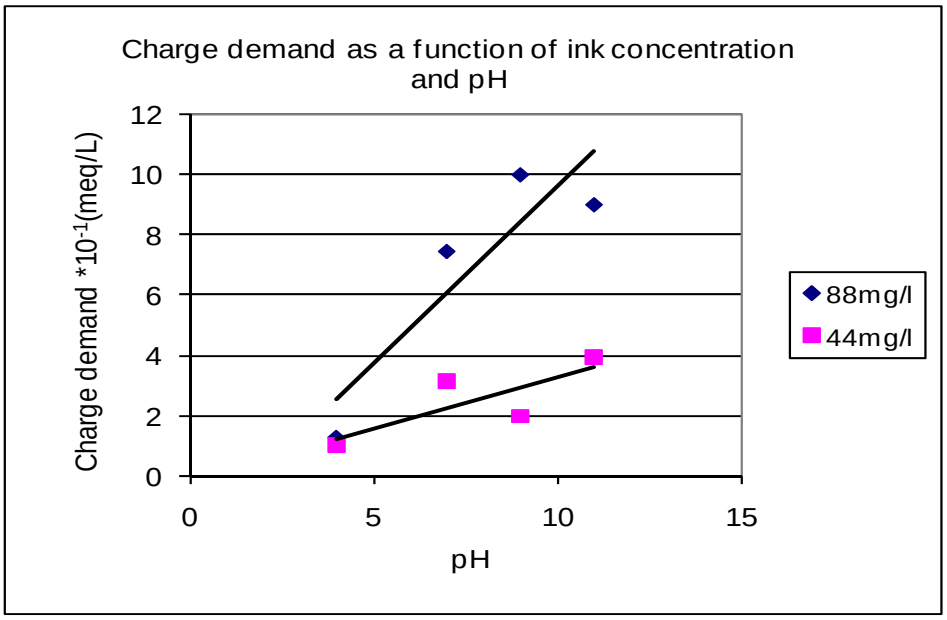

Figure 7-3 Ink Cationic Charge Demand as a function of pH

7.4.1 Copper Electrodes treatment at ink concentration of 44mg/L

Current density and turbidity

The turbidity of the inks dispersion before treatment was about 2500 FAU. The initial turbidity of the non-floated inks decreased with treatment time for both current densities and for all pHs considered. At pH 7 and 9, and for both current densities, the initial turbidity of the non-floated inks after treatment for 20 minutes was the same, about 600 FAU (See Figures 7.4 and Figures 7.6). At 250 mA and pH 11, the initial turbidity of the non-floated inks decreases slightly to 2100 FAU, and the final turbidity was about 1650 FAU. However, at 400 mA and pH 11, the initial and final turbidity only decreases to 850 FAU after 20 minutes of treatment. While, at pH 4, after treatment for 20 minutes the initial turbidity of non-floated inks was 650 FAU and 1500 FAU at currents 250 mA and 400 mA respectively. However, the final turbidity of the non-floated inks was 250 FAU at both currents. The higher initial turbidity of 1500 FAU at 400 mA may come from an excess of metals ions in the solution due to corrosion of copper electrodes at pH 4.

At 400 mA, after treatment for 40 minutes, the initial and final turbidity of non-floated ink is higher than at 20 minutes. The higher turbidity may be due to corrosion of the copper electrodes. At 250 mA, the initial and final turbidity at both treatment time of 20 minutes and 40 minutes is comparable. Corrosion of the copper electrode is higher at higher current density.

Higher current density destabilized the ink more, at least for the treatment condition considered. Once the inks are destabilized they easily float or sediment. The clear supernatant

of the non-floated ink solution indicated by a lower final turbidity (i.e. turbidity after 30 minutes of settling) values demonstrates the destabilizing effect of the treatment. Destabilization leads to agglomeration and precipitation of the ink dispersion. The agglomerated ink settles due to gravitational forces.

The percentage change between the initial and final turbidity reflects the destabilization of inks dispersion and the degree of clarification that occurred during treatment. At 0 minutes (i.e. before treatment) the percent change in turbidity is zero, which indicates that the ink dispersion is stable. Therefore, they do not settle because Brownian motion is in play (Figure 7.8). Also at 0 minutes the degree of clarification is non-existent. At current density of 400 mA, and pH of 4, 7, and 9, percent change in turbidity of the samples collected at treatment time of 20 minutes, was as much as 85% (see Figure 7.8). The percent change in turbidity declines slightly after 20 minutes, because most of the ink dispersion has already been clarified by electroflotation. At pH 11, the turbidity of sample collected did not change more than 10%; the low percent change of turbidity of sample collected indicates stable ink dispersions and low degree of clarification.

At current density of 250 mA, percent change of turbidity of 65% was achieved for both pH 7 and pH 4 after 20 minutes of treatment. Whereas at pH 9 and pH 11, the percent change in turbidity is less than 22% after 20 minutes of treatment. At pH 9, the percent change in turbidity of the collected sample continues to increase to 65% after 40 minutes of treatment. At pH 11, the percent change in turbidity decreases slightly after 20 minute.

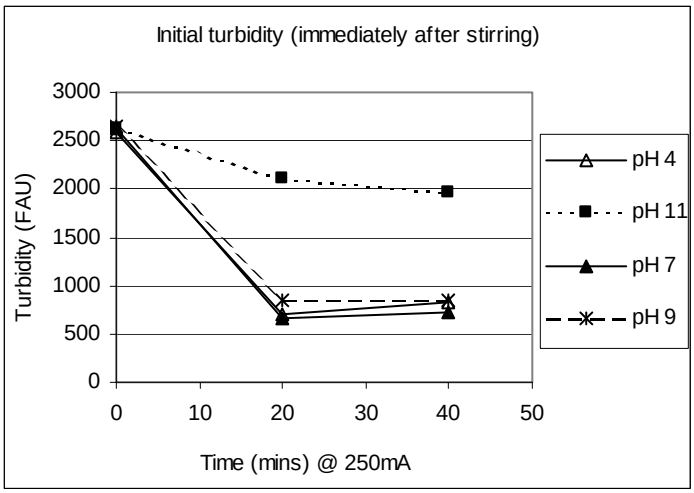

Figure 7-4 Initial Turbidity as a function of treatment time @ 250 mA

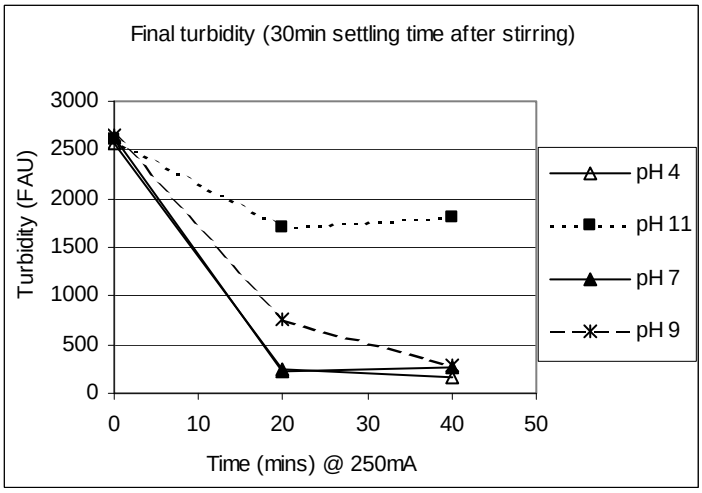

Figure 7-5 Final Turbidity as a function of treatment time @ 250 mA

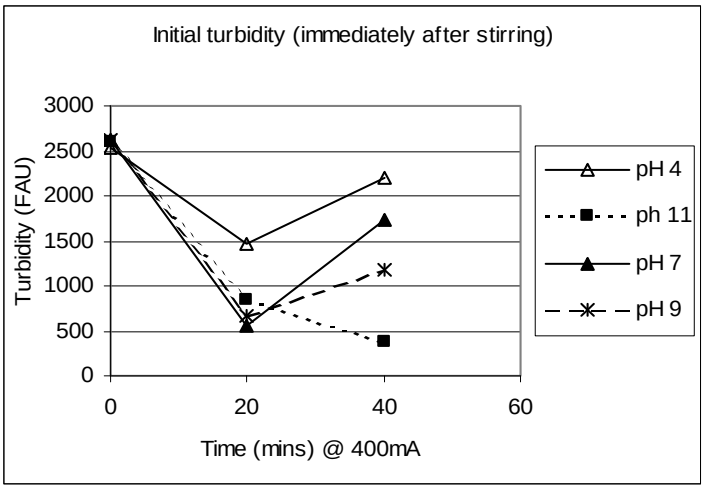

Figure 7-6 Initial Turbidity as a function of treatment time @ 400 mA

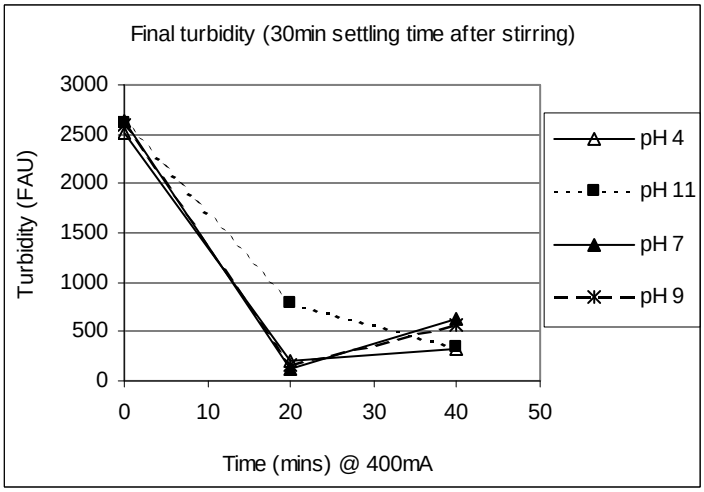

Figure 7-7 Final Turbidity as a function of treatment time @ 400 mA

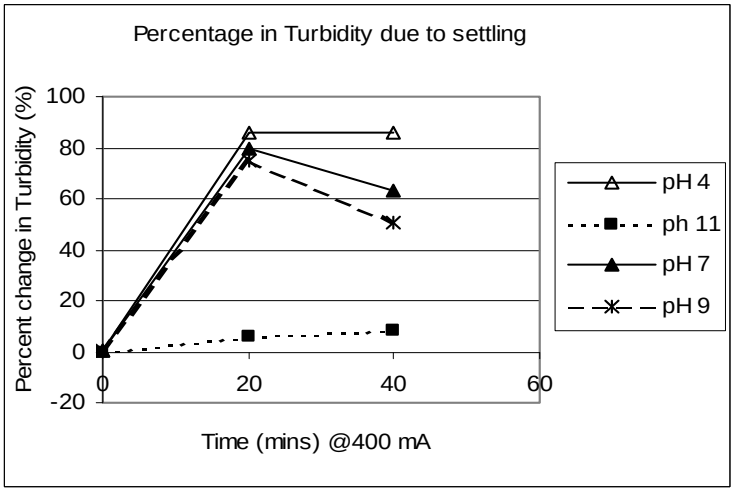

Figure 7-8 Percent change in Turbidity @ 400 mA

Cationic demand

Cationic demand measures the total charge of the ink dispersion. The total charge of the ink dispersion is a function of the concentration of the ink dispersions and the degree of ionization of the polyelectrolyte and particles in a solution. At 250 mA, and at both pH 7 and pH 4, the turbidity of the non-floated ink dispersion is comparable at all treatment times (see Figures 7.4 and 7.5). However, the cationic demand at pH 7 and pH 4 are different (Figure 7.9). The difference is a result of the degree of ionization of the ink particles. At pH 4, the polyelectrolytes on the carbon particle are protonated by hydrogen ions, but at pH 7, the degree of protonation is less. For both current densities of 250 mA and 400 mA, the cationic demand was highest and lowest at pH 11 and pH 4 at all treatment times. The reduced cationic demand at pH 4 is not only due to the reduction of non-floated ink dispersion concentration but is also due to the degree of ionization of the polyelectrolyte. The polyelectrolytes are protonated at acidic pH; therefore the cationic demand will be less.

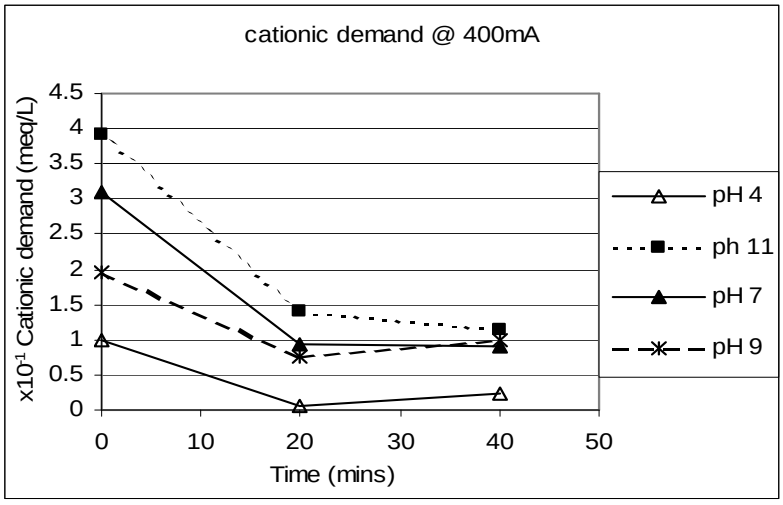

Figure 7-9 Cationic Demand as a function of treatment time @ 400 mA

7.4.2 Aluminum electrode treatment at ink concentration of 88 mg/L

The electrochemical cell was used to treat the model flexographic ink dispersion at a higher ink concentration of 88 mg/L. An aluminum electrode was used as the anode instead of a copper electrode.

At 400 mA, and at all pH levels, the average initial turbidity of the sample before treatment is about 3448 FAU (standard deviation of 115, see Figure 7.10). For both current 250 mA and 400 mA (current densities of 13.73 A/m^2 and 21.9 A/m^2respectively) and at pH 4, the initial turbidity of non-floated ink dispersion decreases more rapidly than at any other pH level (See Figures 7.10 and 7.11). At pH 4, the initial turbidity was 500 FAU and 1100 FAU for current density of 400 mA and 250 mA respectively after 20 minutes of treatment.

At pH 11, and for current density of 250 mA, the initial turbidity of 3500 FAU changed slightly with treatment time. This means that most of the ink dispersion was not floated, however, at current density of 400 mA; the initial turbidity did change to 2500 FAU after 20 minutes of treatment. The decline in turbidity with treatment time was more rapid at higher current density. For 400 mA, the initial turbidity of the non-floated sample was lower at pH 4 than at pH 7 after 20 minutes of treatment, but their final turbidity was the same. The degree of settling of the non-floated fraction of ink is reflected in the percent change of turbidity between the initial turbidity and the final turbidity of the treated sample after settling. For 400 mA, after treatment of 20 minutes, percent change of turbidity was 85%, 50%, 30% and 10%, at pH 7, pH4, pH 9 and pH 11 respectively (Figures 7.10, 7.12 and 7.14).

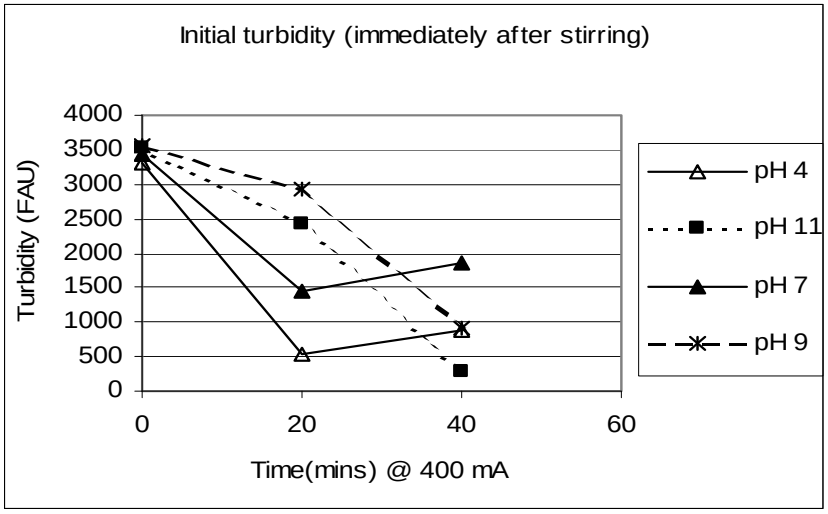

Figure 7-10 Initial Turbidity as a function of treatment time @ 400 mA. Aluminum electrode and 88 mg/L ink concentration.

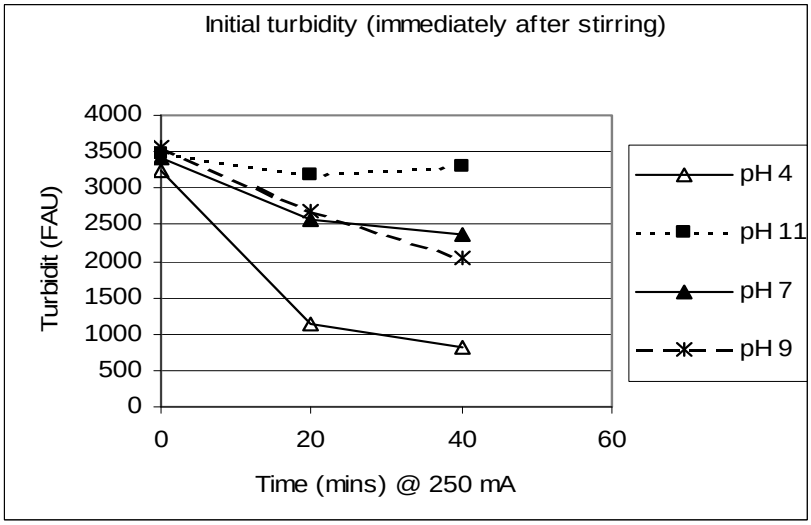

Figure 7-11 Initial Turbidity as a function of treatment time @ 250 mA. Aluminum electrode and 88 mg/L ink concentration.

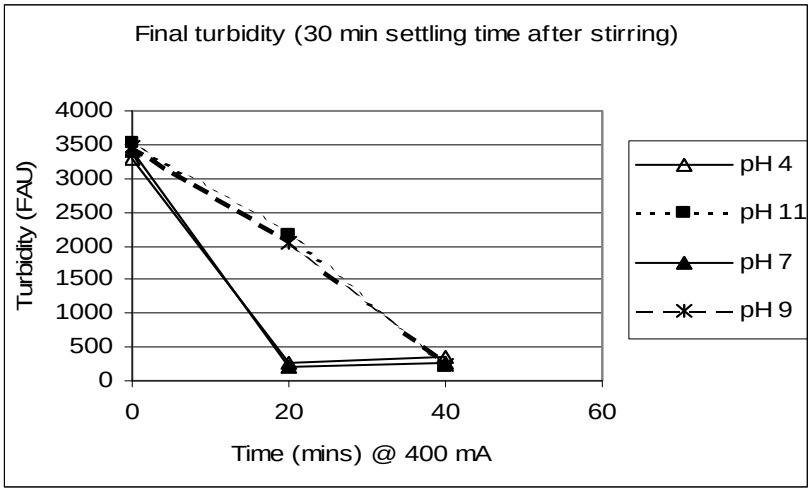

Figure 7-12 Final Turbidity as a function of treatment time @ 400mA. Aluminum electrode and 88 mg/L ink concentration.

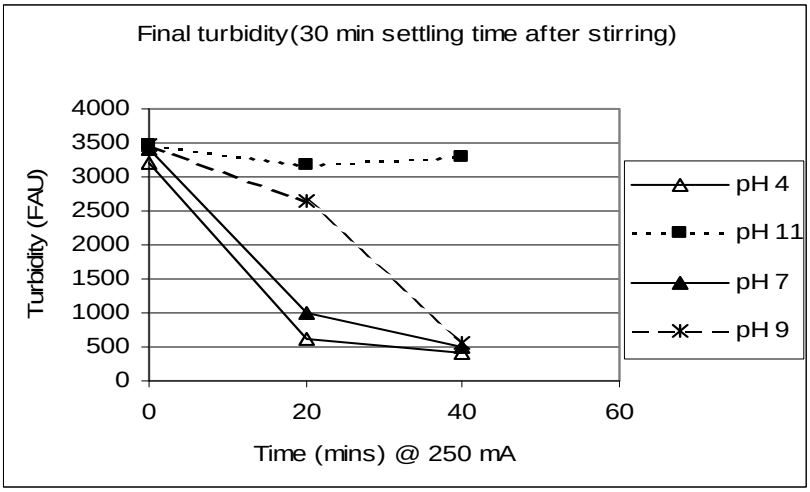

Figure 7-13 Final Turbidity as a function of treatment time @ 250mA. Aluminum electrode and 88 mg/L ink concentration.

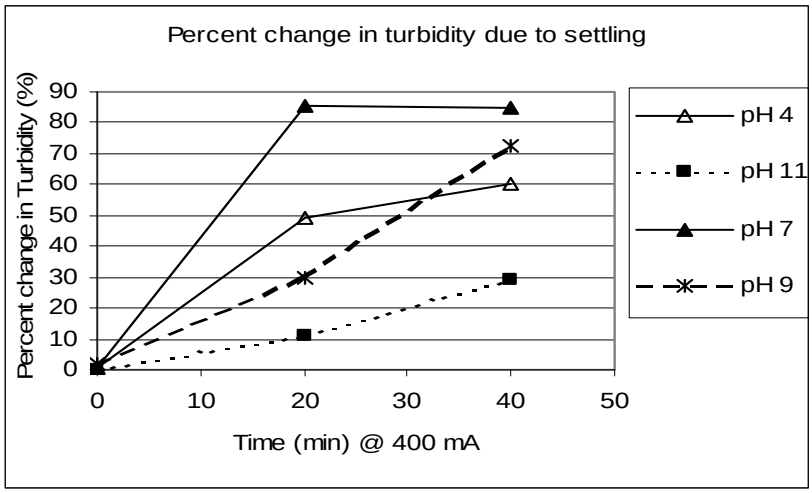

Figure 7-14 Percent reduction in Turbidity @ 400mA. Aluminum electrode and 88 mg/L ink concentration.

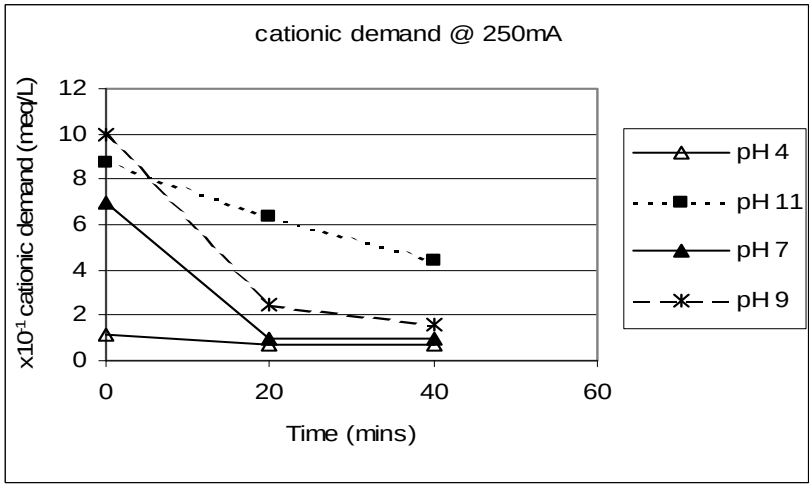

Figure 7-15 Cationic demand as a function of treatment time @ 250mA. Aluminum electrode and 88 mg/L ink concentration.

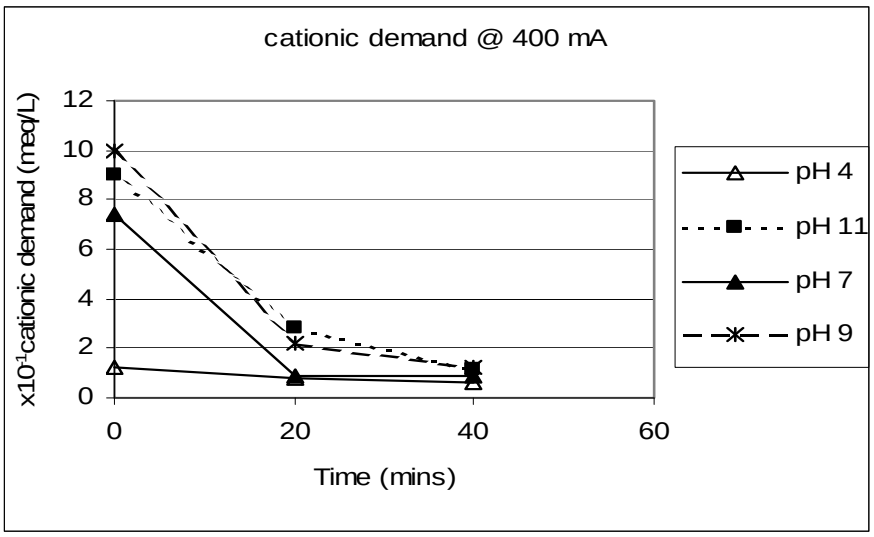

Figure 7-16 Cationic demand as a function of treatment time @ 400mA. Aluminum electrode and 88 mg/L ink concentration.

Cationic Demand

At both current densities, the cationic demand for the untreated sample was different at all pH levels (see Figures 7.15 and 7.16). The cationic demand was lowest at pH 4. Also at 20 minutes, the cationic demand of the non-floated sample was the same for pH 4 and pH 7. At 400 mA, the cationic demand for the sample at different pH was similar after 40 minutes of treatment, which indicates the concentration of the ink dispersion in the non-floated sample has been reduced. At 250 mA, the cationic demand at 40 minutes was about 0.08 meq/L, and was the same for all pH conditions except at pH 11, which was 0.42 meq/L. The cationic demand of the untreated ink dispersion doubled when the concentration of the ink was doubled (see Figures 7.3).

7.4.3 Aluminum electrode treatment of wash deinking filtrate

Table 7-2.Turbidity of Wash deinking filtrate treated with electrochemical cell using aluminum cathode

Treatment time (min)		0	0	20	20	40	40
pH	Current	*After settling*	*Before settling*	*After settling*	*Before settling*	*After settling*	*Before settling*
				TURBIDITY (FAU)			
4		442	495	61	344	52	275
7	125mA	496	513	52	241	52	248
9		659	695	519	641	115	551
11		203	487	142	241	63	89
4		412	481	27	66	16	18
7	250mA	557	609	91	413	10	18
9		618	660	96	518	31	389
11		208	466	65	115	51	90

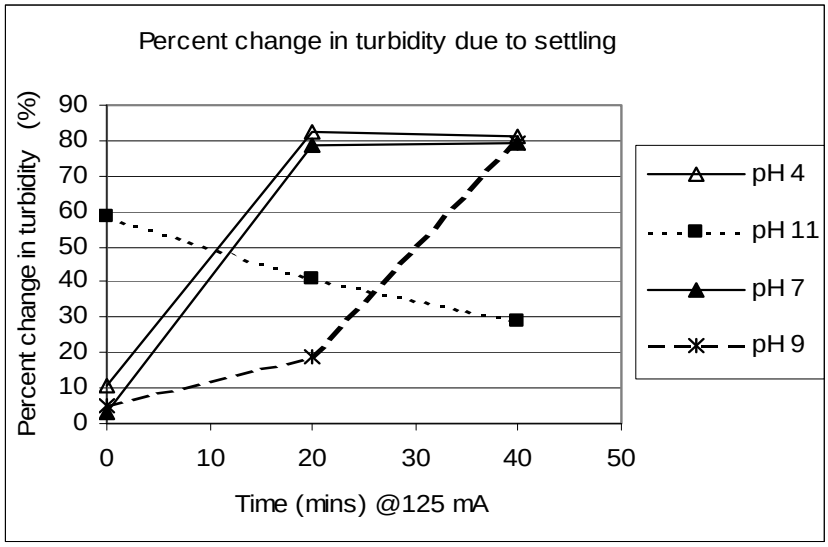

Figure 7-17. Percent change in Turbidity as function of treatment time @ 125 mA

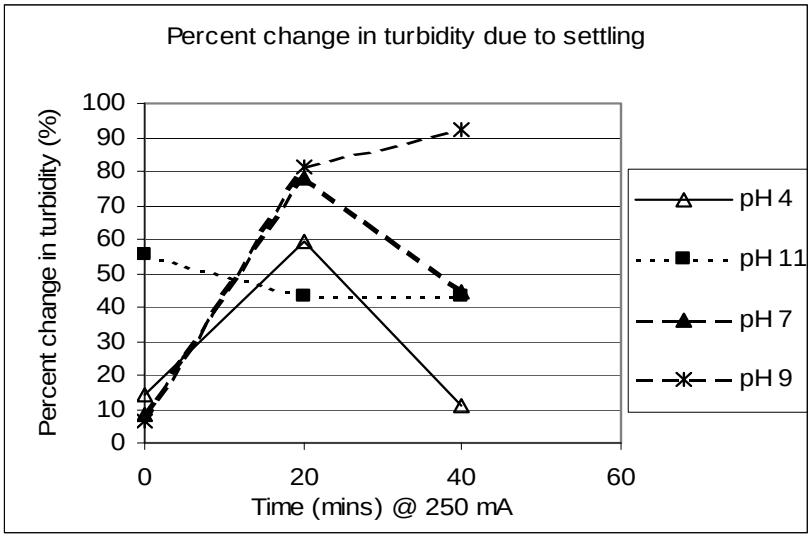

Figure 7-18 Percent change in Turbidity as a function of treatment time @ 250mA

Current density and turbidity

Unlike the model ink dispersions where the turbidity of the untreated samples was the same at all pH levels, the untreated sample of the wash filtrate varied with the pH levels (see Table 7.2, Figures 7.4, 7.6, 7.10, & 7.11). The turbidity of the untreated sample at 125 mA, and at pH 4, pH 11, pH 7 and pH 9 were 495 FAU, 487 FAU, 513 FAU and 695 FAU respectively. The turbidity of the untreated wash filtrate was highest at pH 9; this may be because this filtrate required the least amount of (sodium hydroxide) to adjust the pH.

At pH 11, the percent change in turbidity (i.e. changes of initial and final turbidity) for the untreated wash filtrated was 56% (See Figures 7.17, 7.18). At pH 4, pH 7, and pH 9 the percent change in turbidity was 12.5%, 5.9%, and 5.7% respectively. For the model ink dispersions, the percent change in turbidity of the untreated sample was less than 2% for all pH levels (See Figure 7.8).

The cationic demand varied with pH. In general, the cationic demand was highest at pH 11 and lowest for pH 4 (See Table 7.3). The cationic demand of the non-floated ink decreased slightly with treatment time. The cationic demand for the untreated filtrate was less when compared to the untreated model ink dispersions at both concentrations. (See Table 7.3 and Figure 7.3)

Table 7-3.Cationic demand of wash filtrate treatment electrochemical cell

*Cationic demand *10^{-1} (meq/L)*				*Cationic demand *10^{-1} (me q/L)*			
125 mA	Time			250 mA	Time		
pH	0	20	40	pH	0	20	40
4	0.599	0.6988	0.349	4	0.5793	0.3016	0.3626
7	1.0132	0.5973	0.6471	7	1.0204	0.6143	0.6172
9	1.3746	0.8687	0.6949	9	1.4456	0.5998	1.611
11	0.9323	0.8903	0.7968	11	0.9986	0.9371	0.9205

7.5 Discussion

The polyacrylic resin acts as a dispersant for carbon black particle, and gives the subsequent ink dispersion the right stability and rheology for printing. The polyacrylic acid resin or polyelectrolyte help to stabilized the carbon black particles. The stability is due to electrostatic repulsion and the steric hindrance mechanism.[10] Electrostatic repulsion induced stabilization is largely removed at high ionic strength and low degree of neutralization. If the stabilization persists under high ionic strength and or low degree of ionization, then the principal mechanism of stabilization should be steric in origin.[11] Steric stabilization is cause

by unfavorable thermodynamic interaction between polyelectrolyte molecules adsorbed on adjacent particles

Both the model flexographic inks and wash deinking filtrate suspensions from flexographic newsprint pulp slurry were decontaminated (or clarified) using an electrochemical cell.

The degree of decreasing turbidity is a strong function of pH and current density. For example, at pH 4, the turbidity of the 88 mg/L ink dispersion decreased by 80% and 92% at current densities of 250 mA and 400 mA respectively after 20 minutes of treatment (see Figure 7.16). Also, at pH11, the turbidity of the 88 mg/L ink dispersion decreased by 8% and 41% at current density of 250 mA and 400 mA respectively after 20 minutes of treatment.

First, at pH 4 and pH 11, the degree of ionization of the polyelectrolyte in the ink dispersion is different. Their respective cationic demand of the untreated ink dispersion is 0.118 meq/L and 0.874 meq/L and is due to the different degree of ionization. Fernandez et al showed that the zeta potential of two types of model inks changed from slightly positive to more negative as the pH was changed from acidic to alkaline. Zeta potential is closely related to the electrical double-layer repulsion between particles. Larger values will usually indicate a stable dispersion. The larger (more negative) the zeta potential of an ink dispersion, the larger the cationic demand. The lower decrease of turbidity of 8% at pH 11 compared to 80% at pH 4 is due to the higher stable ink dispersion at pH 11.

Secondly, higher current density causes a higher decrease in the turbidity of ink dispersion. In an electrochemical cell, higher current generates more gas bubbles by the electrolysis of water. The electrochemical reactions at the cathode and anode are hydrogen

evolution and oxygen evolutions reactions, respectively [4 12 9]. In addition, the supply of current to the electrochemical cell also determines the amount of Al^{3+} ions released from the electrodes. The nascent Al^{3+} ions are very efficient coagulants for particulate flocculation. Fukui used aluminum ions sulfate as a coagulant in the electro-flotation of blue ink in concentration of 10^{-3} m^3/m^3.[13] The collection of the blue ink increased with current density. The higher number of bubbles and the higher metal ions released at higher current is responsible for better reduction in turbidity.

A lower concentration (44 mg/L) of the model ink dispersion was treated with an electrochemical cell, albeit with a different electrode, Copper anode. Consequently, Cu^{2+} ions are release from the electrode. At pH 4, the turbidity of the 44 mg/L ink dispersion decreased by 90% and 92% at current density of 250 mA and 400 mA respectively after 20 minutes of treatment. Also, at pH 11, the turbidity of the 44 mg/L ink dispersion decreased by 35% and 69% at current density of 250 mA and 400 mA respectively after 20 minutes of treatment. The current density and pH has the same effect on the ink dispersion, like in the aluminum case, even though a lower concentration and a copper electrode were used in the treatment. A wash filtrated obtained from screening flexographic newsprint pulp slurry was also treated with the electrochemical cell. This electrochemical cell electrode's setup is the same as the one used to treat the model ink of 88 mg/L. At pH 11, the untreated wash filtrate had a 60% percentage change in turbidity (see Table 7.3). While at pH 7, the percentage change in turbidity was only 8%. This change indicated that adjusting to pH 11 using sodium hydroxide causes the wash filtrated to coagulate and precipitate, before electrochemical treatment. The precipitation may be due to the action of positive sodium salt ions on the polyacrylic resins of inks. The zeta potential curve as a function of pH as been reported to show a minimum i.e. as

the zeta potential becomes negative going from acidic to alkaline solution conditions, but as the solution becomes more alkaline the zeta becomes less negative[14]. Addition of excessive positive sodium ions increases the ionic strength and screens the electrostatic repulsion. At pH 11, the conductivity, which is measure of dissolved ions, is at the highest and does not change with treatment time. (See Table A.2.). The conductivity of the wash filtrate was higher compared to other values from the model ink dispersion.

For the wash filtrate treatment at 250 mA, after 40 minutes the initial turbidity (measured immediately after sample is collected) was 389 FAU, 90 FAU, 18 FAU, and 18 FAU at pH 9, 11, 4, and 7 respectively. While the final turbidity (the collected sample measured after 30 minutes of settling) were 31 FAU, 51 FAU, 16 FAU, and 10 FAU respectively. After 40 minutes treatment times, all the final turbidities of the non-floated inks were less than 51 FAU (see Table 7.2).

In general, the difference between the initial and final turbidity indicates the degree of sedimentation. Stable dispersions of colloidal particles will sediment at the onset of destabilization. Destabilization occurs during treatment, however, no settling was observed during treatment because the solution was stirred continuously. Once treatment was completed and stirring stopped, sedimentation occurred. During treatment, particles destabilized and gas bubbles generated by electrolysis removed the coagulated inks. The collision between bubbles and the coagulated inks was promoted by stirring. The solution was relatively quiescent since the stirring intensity was low.

The particle size is also expected to increase with electrochemical treatment, since the aluminum ions destabilized the inks and caused coagulation. Larsson et al showed that the removal of model ink particles increased with particle size[15]. Fukui et al, also reported an

increase in particle size, but attributed it to bubbles induced by coagulation. Because larger particles sediment rapidly, the turbidity of the supernatant is low. The reduction in turbidity corroborates the increased particle size due to the agglomeration of the colloid particles.

In alkaline conditions, destabilization and clarification was observed. Also in alkaline conditions, the effluent pH increased with treatment time. This effect rules out the protonation of carboxylic groups of the poly acrylic acid on the carbon black as the mechanism for destabilization. Destabilization is induced by the release of aluminum ions or copper ions from their respective electrodes. The pHs measured after treatment were at least 0.5 higher than those before treatment. The increase of pH at acidic conditions has been attributed to the hydrogen evolution. In this study an increase in pH is also observed in alkaline conditions during treatment.

However, in acidic or at lower pH, carboxylic groups are protonated, which results in the reduction of the solubility of the carbon black dispersion. Therefore, destabilization is partly due to protonation and partly due to coagulation because of the presence of metal ions.

The pH at which the dispersion of flexographic inks streaming charge value becomes zero is called point of zero charge (PZC). For flexographic ink dispersion, the PZC would occur in very acidic conditions of pH 1 and pH 2[16]. The lowest pH considered in this study was pH 4; therefore dispersion of inks was at least partly negatively charged. At acidic conditions the carboxylic groups on the polyelectrolytes are protonated. Once these polyelectrolytes are protonated, their solubility is reduced, causing carbon black to which they are adsorbed to precipitate and coagulate.

Fernandez et al studied the effect of various salts on the coagulation of flexographic ink dispersion. The critical coagulation concentration (CCC) is the concentration of counter ions that is needed to induce coagulation. The higher the valency of the ions, the lower the CCC (the concentration needed to reach a turbidity of 200 NTU) needed to induce coagulation. The ionic strength is also high for higher valence counter ions. Adding counter ions or changing the pH can change the total charge of a colloidal and ionic solution.

Fernandez et al reported that the CCC of $CaCl_2$ needed for 440 mg/L carbon black dispersion was higher at pH 10 than at pH 4. Dorris et al reported a marked shift towards a large particle size for 40 mg/L carbon black dispersion at the addition of 1000 mg/L $CaCl_2$ in the presence of sodium oleate at pH 8[17].

Fernandez also showed the concentration of salts at the isoelectric point of the flexographic inks dispersion is lower than lower the CCC[4]. The concentration of salts, which reduce or eliminate the electrostatic repulsion, may not be able to destabilize the ink because they are also sterically stabilized.

The concentration of counter ions to induce coagulation is higher at alkaline conditions than at acidic conditions. For example, at pH 4, the turbidity of the 88 mg/L ink dispersion decreased by 80% and 92% at current density of 250 mA and 400 mA respectively after 20 minutes of treatment (See Figures 7.10, 7.11). The higher current density released more metal ions.

Also, at pH 11, the turbidity of the 88 mg/L ink dispersion decreased by 8% and 41% at current density of 250 mA and 400 mA respectively after 20 minutes of treatment. For the same current density only a small decrease in turbidity is achieved compared to pH 4.

The aluminum electrodes release aluminum ions. Aluminum ions exist in different species at various pHs. Between pH 4 and 5.5, the ions exist predominately in the aluminum hydroxyl complexes ($AlOH^{2+}$ & $Al(OH)_2^{+}$) and the positively charged $Al(OH)_3$, which is predominant in the pH range between 5.5 and 7.8. These species are adsorbed on the inks. Above pH 7.8, aluminum hydroxide has a negative potential[18 19]. At pH 4 and pH 7 flotation of model flexographic ink is higher at these values than the other pH values on Figures 7.10, 7.11, 7.12, and 7.13.

The presence of metals ions is reported to also shift the PZC of ink dispersion from more acidic pH towards neutral pH[20]. Because metals ions can shift the PZC, the reversal of electrostatic charge need not occur by protonation of polyelectrolyte by hydrogen ions but can also occur by the sorption of metals on the polyelectrolyte.

The formation of stable bubbles in a latex–polyacrylic stabilized dispersion at acidic pH as also been reported[21]. Binks et al showed that foams can be prepared and stabilized only at pH values below the isoelectric point where particles are both uncharged and flocculated or acquire a positive charge. The hydrophobicity of these particles is sensitive to pH and enables the particles to be well held at the air-water surfaces. The increased collection of the model ink dispersion at a lower pH may also be related to the increase hydrophobicity of the inks at a lower pH (see pH 4 and pH 7 on Figures 7.10, 7.11, 7.12, and 7.13). The hydrophobic particles adhere to the air-water interfaces forming stable bubbles. Stable bubbles give better froth formation and more collection of the ink particles.

A directly comparison of copper, aluminum and stainless steel anode, show that stainless steel does not induce coagulation, thus the turbidity stays the same throughout the

treatment time (see Table 7.4). The sample turbidity decreased when Aluminum and copper electrode was used indicating coagulation and flotation. The copper electrode gave the lowest the turbidity after treatment, indicating that the nascent copper ions are more effective coagulating agent. The decontamination efficiency, i.e. the ratio of the change in turbidity and the initial turbidity, are 76%, 61% and 2% for the copper, aluminum and stainless steel anode respectively. Aluminum ions have higher valency number than copper ions, but copper ions have been reported to form stable complexes than other divalent and trivalent metal ions, and it possesses higher affinity for carboxylic acids.[22]

A separate wash filtrate was treated with an electrochemical cell with an aluminum cathode and a stainless steel anode. The hardness of the treated sample was more than 100 times more than the hardness of the untreated sample (see Table 7.5). The increase in hardness was expected because metal ions from the electrode had been released into the solution. Hardness is a measure of metal ions content. This content usually consists of high levels of divalent and trivalent metal ions, mainly calcium and magnesium, but include several other metals as well, such as aluminum, iron and manganese. Water hardness is reported as mg/L of calcium carbonate ($CaCO_3$). The in situ generation of aluminum ions from the electrodes contributes to the total hardness of the treated solution. Finally, a benefit of electrochemical cell treatment is that it reduces COD (see Table 7.5).

Table 7-4. Aluminum, Copper and Stainless steel anode comparison. Sample ink concentration was 0.065 mg/cm^3 at pH 7. Treated at 250 mA.

Anode	*Cathode*	*Treatment time (minutes)*	*Turbidity (FAU) (**before**/after 30 minutes of settling)*	*pH*	*Conductivity (μs)*	*Cationic demand *10^{-1} (meq/L)*
Aluminum	Stainless steel	0	**2918**/2923	6.8	138	0.75
		10	**2546**/2513	7.3	145	0.34
		20	**1128**/830	8.1	139	0.27
Copper		0	**2830**/2877	6.9	139	0.83
		10	**2913**/2853	7.5	140	0.26
		20	**690**/500	8.5	135	0.28
Stainless steel		0	**2887**/2903	6.9	139	0.73
		10	**2981**/2925	6.9	140	0.72
		20	**2792**/2863	6.9	140	0.77

Table 7-5 pH, COD and turbidity of wash deinking filtrate

	Treated water (filtered)	*Untreated water*
Conductivity (μs)	0.442	0.508
COD (mg/l)	0	63
Hardness ($CaCO_3$ mg/l)	700	40
Streaming potential (mV)	-303	-478
Cationic Charge demand (meq/l)	0.0214	0.386
pH	9.42	8.18

7.6 Conclusion

Unlike the model ink dispersions where the turbidity of the untreated samples, was the same at all pH levels, the untreated sample of the wash filtrate varied with the pH levels

The degree of decontamination is a strong function of pH and current density. The pH affects the degree of ionization, which is measured by cationic charge demand. At pH 4, the turbidity of the 88 mg/L ink dispersion decreased by 80% and 92% at current densities of 250 mA and 400 mA respectively after 20 minutes of treatment. Also, at pH11, the turbidity of the 88 mg/l ink dispersion decreased by 8% and 41% at current density of 250 mA and 400 mA respectively after 20 minutes of treatment.

A direct comparison of copper, aluminum, stainless steel electrode, shows that their respective decontamination efficiency, reported as the percent change in turbidity, decreases by 76%, 61% and 4% respectively

The treated decontaminated water has 60 less COD than the untreated water. The treated also has higher hardness values indicating the presence of nascent metal cations release from the electrodes.

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CHAPTER 8 : PROPOSED COMPLETE TREATMENT

8.1 Introduction

Conventional flotation deinking mill were design to deink oil-based offset ONP and OMG. An introduction of as little as 5% flexo-ONP into the furnish may upset the deinking operation because the flexo inks are hydrophilic and sub micron size, with an average size of 0.5 microns as opposed to hydrophobic inks which has average size of 20microns.

Feed furnish that does not contain flexo-ONP as on average 45% brightness and ERIC of 1200 ppm and a after flotation brightness of 57%. [1 2]

A furnish containing 15%, 30% and 100% flexographic ONP have a brightness of 37%, 37% and 32% respectively.[3 4] Galland also reported that a 100% flexo–ONP had a feed ERIC value of 2000 ppm for acidic pulping and as high as 5000pm for alkaline pulping conditions. After flotation, the accept ERIC values were 1500ppm and 3500ppm respectively.

In deinking mills, the Deinked pulp (DIP) target is an Effective Residual Ink Concentration (ERIC) value of 235 ppm. The 235 ppm ERIC value corresponds to a brightness of about 58%. [5]. Reaching the target ERIC 235 ppm from a starting ERIC of 5000 ppm could be challenging.

Putz et al reported that during flotation, the brightness gain for a 100% flexographic-ONP is comparable those obtained for furnish that contain offset and letterpress printed-paper[4]. However, because the undeinked flexographic-ONP starting brightness is lower compared to the others, its final brightness is not acceptable. Putz et al found that the brightness after de-inking exclusive by washing of letterpress, offset and flexo printed newspapers is almost the same, having a 52% on average. There is however a lower yield

with washing. Besides, the washing deinking does not contribute to solving the problem of the deinking of water-based flexo news. Owing to the fact that the clarification of the wash water is inefficient, the reuse of the polluted wash water is a drawback for the application to this wash process. In order to cope with a 100% flexographic-ONP feed, a combination of treatment methods is proposed.

A method that uses a new water clarification process.

In this chapter, a kinetic model is used to describe the pulping or slushing step. Slushing is followed in the flotation deinking; an electric field technology is incorporated to improve the deinking efficiency. Thereafter, the flotation accept is screen-washed and a subsequent clarification of the filtrate with an electric field in a process called electroflotation. The water clarification treatment requires no addition of chemical or external gas bubbles. The clarified water can be recycled to the water stream of the deinking mill

8.2 Process and materials used

Pulping kinetics

Material used: Furnish 100% flexographic ONP (Macon Telegraph Newspaper)

Complete treatment solution

Material used: Furnish 100% flexographic ONP (Macon Telegraph Newspaper)

Washing

In the washing step the 1% consistency stock is thickened to 8% consistency using a screen. Screen size 150 mesh, opening size is roughly 104 microns

Water clarification

Electrochemical cell volume capacity is 6,000 liters. Electrodes used stainless steel and aluminum electrodes were used and the power source described in chapter 2 and chapter 5. The water clarification treatment time lasted 40 minutes. A filtration process using a filter paper and a vacuum system follows the water clarification.

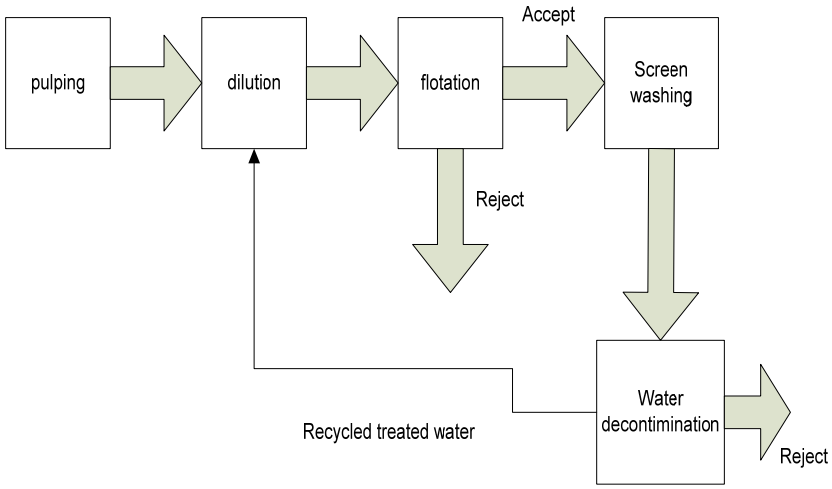

Figure 8-1 Complete treatment flowchart

8.3 Pulping

Inks consist of solvents, binders and pigment. During printing on paper, these solvents are evaporates and the binders and pigment are attached to the paper. To detach these inks from the fiber, the fiber undergoes a pulping process. The pulping process usually involves soaking the paper in water with de-inking chemicals and the mixtures is agitated at high speed. The applied energy causes the paper to de-fiber consequently liberating the ink. Some ink like flexographic are easily solubilized in water thus only the smallest amount of energy is needed to free up the ink. The ink distribute between the water phase and fiber phase. Comparison has been made between detergency and de-inking[6]. Like pulping, detergency or laundering can be considered as a prototypical example of the problem of removing particulate from adhering surfaces. It can be defined as the removal of unwanted substances from a solid surface immersed in a medium, generally through the application of a mechanical force, in the presence of a chemical substance. In both cases, the object is to remove particle contaminates adhering to a surface.

The process of deinking 100% flexographic-ONP starts with pulping. A complete treatment for this newsprint type is proposed in figure 6.1.

8.3.1 Langmuir kinetics

Nesbit studied the effects of pH, re-pulping time, and re-pulping power on flexographic ink detachment and redeposition on a model re-pulping system.[7] The ink's carbon content determined by Thermogravimetric Analysis (TGA) and brightness was used to measure the degree of detachment and redeposition during re-pulping of printed-paper. The

carbon content data collected from Nesbit experiments did not fit Langmuir equation. But the Langmuir model was used to fit data (adopted from Ciampa's work-using ERIC data) from acidic re-pulping experiments during which previously printed, dried, and ground ink was added to de-fibred newsprint that has never been printed. In this current study, turbidity data was used to fit into the Langmuir model.

When particles are added into a fiber suspension, the particles can deposit on fibers until the full surface of the fibers coated. Let the total number of particles that can deposit on the fibers (per unit volume) be N_{max} and the number initially present in suspension N_o. Assuming Langmuir kinetics, the number of inks N on the fiber at time, t is described

$$\frac{dN}{dt} = \alpha k_o N_c N_f \left(1 - \frac{N}{N_{\max}}\right) - k_{def} N$$

and can be written in the dimensionless form,

$$\tau_{dep} = \frac{1}{\alpha k_o N_f}, \quad \tau_{esc} = \frac{1}{k_{\det}}$$

$$\frac{d\theta}{dt} = \frac{1}{\tau_{dep}}(n_o - \theta)(1-\theta) - \frac{\theta}{\tau_{esc}}$$

$$n_0 = \frac{N_o}{\Gamma^*_{\max}} \quad \theta = \frac{\Gamma^*_{ext}(t)}{\Gamma^*_{\max}}$$

$$N_o = N_c(t) + \Gamma^*_{ext}(t)$$

where $N_c(t)$ is the number of ink in the outside liquid at time t, Where n_o, represent the ratio of initial amount of particles present and the maximum that can be deposited Γ^*_{max} . θ is the ratio of the amount that is deposited on the fiber, $\Gamma^*_{ext}(t)$ and the maximum amount that can be deposited on 1g of fiber, Γ^*_{max}

The kinetics of deposition and detachment is determined by the two time-constants τ_{esc} and τ_{dep}, which are the time scales for particle escape and deposition.

In pulping of newsprint, instead of particle deposition on the fiber, there is ink detachment and desorption. Figure 8.2 show desorption of ink particles from pulping 100% flexo-ONP. For the first 270 seconds of pulping, desorption of ink particles particle follow the Langmuir kinetics. The calculation of the model and how it correlates with the experimental is explained in the appendix B (see Table B9 and figure B-1). It is estimates that the total amount of ink is 0.082% of the fiber (gram of ink/ per gram of fiber). Typical amount of ink printed on paper is 0.1%.[8]

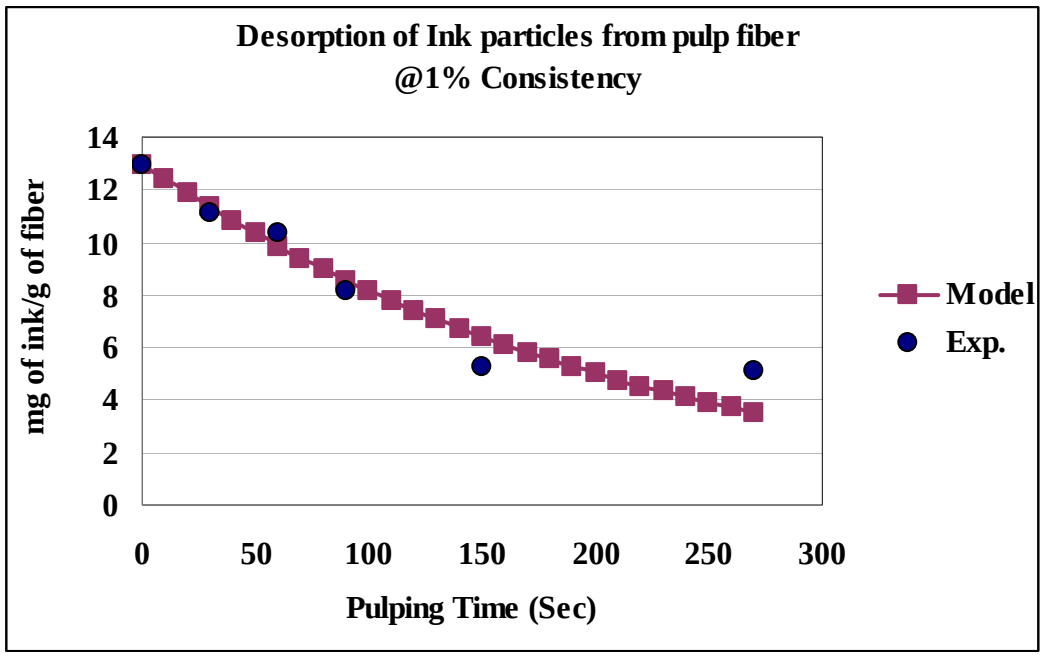

Figure 8-2 Langmuir kinetic at short pulping time, τ_{esc} and τ_{dep} were estimated to be 275s and 600s respectively

The time constant τ_{esc} and τ_{dep} are a function of the hydrodynamic and colloidal interactions between the ink and fiber. τ_{esc} and τ_{dep} were estimated to be 275s and 600s respectively. It was found that equation equivalent to eqn. 1 describe particle deposition on fibers fairly accurately for a number of particles like fillers: Tio2[9], caco3[10], clay[11] as well as the adsorption of polyethyleneimine (PEI)[12]

The time constant is a function of the collision occurs between particles like inks and fibers and the collision efficiency. The collision efficiency is the ratio of the number of collisions leading to deposition or flocculation to the total number of collisions. The number of collisions leading to capture depends on the ratio of colloidal to hydrodynamic forces. The colloidal interactions could be described using the well-known classical DLVO theory. Where the total interaction energy is

$$V_T = (V_{DLR} + V_{LVA})$$

Where V_{dlr} is the repulsive electrostatic double layer and V_{lva} is the attractive van der waal interaction. Repulsive V_{dlr} forces promote detachment and attractive V_{lva} forces promote deposition

Ink detachment occurs during pulping. In subsequent deinking process like flotation, bubbles carries out detach ink particles and bring them to the surface of the cell as froth.

8.4 Flotation deinking

A flotation-deinking vessel contains a water dispersion of ink particles, fiber and fine particles and bubbles. The ink particle could be attached to the fiber or unattached (i.e., free particles).

The first-order reaction equation below has been used to describe flotation of a homogenous particle suspension.[13]

$$\frac{dN_f}{dt} = -kN_f$$ **Equation 8-1**

Where N_f is total amount of free particles, k is the rate constant, and is equal to:

$$k = \frac{1}{4} S_b P .$$

Where P is the probability of collection, i.e. the product of the probabilities of particle-bubble collision, attachment and stabilization against external stress forces. S_p is the amount of air bubbles

Yoon *et al* has related *k* to surface force and hydrodynamic forces acting on the ink-bubble interaction [14]. N_f is differentiated from ink adsorbed on fiber and inside the fiber lumen. Equation 1. becomes

$$N_f = N_{fo} e^{-kt}$$

A flotation of mixture of flexo-ONP/OMG mixture was done at different float times. The results are summarized on Table 8.1. The rate constant was -0.0289 (see Figure 8.3). Once the rate constant is known, N_f can be estimated for a given N_{fo} and time. The flotation rate constant depends on the ONP type, frothing agents, surfactants, the height and volume of pulp slurry in the float cell, consistency, and airflow rate. The rate constant for the offset-ONP would be higher since the % ERIC removal is higher than for flexo-ONP. A first order may be appropriate to describe flotation of flexo-ONP.

Table 8-1 Flotation kinetics, Feed and Accept ERIC, solid and fiber loss

Float time (min)	*LN (Accept ERIC)*	*Feed ERIC*	*Accept ERIC*	*% ERIC Removal*	*% Total Solid loss*	*% Fiber Loss*	*Total Reject (g)*	*Water Loss (g)*
8	8.02	4028	3033.4	24.69	13.31	8.80	5.15	376.9
5	8.13	4028	3395.4	15.69	10.86	7.18	3.92	326.6
3	8.16	4028	3491.9	13.29	6.69	4.38	2.71	237.3

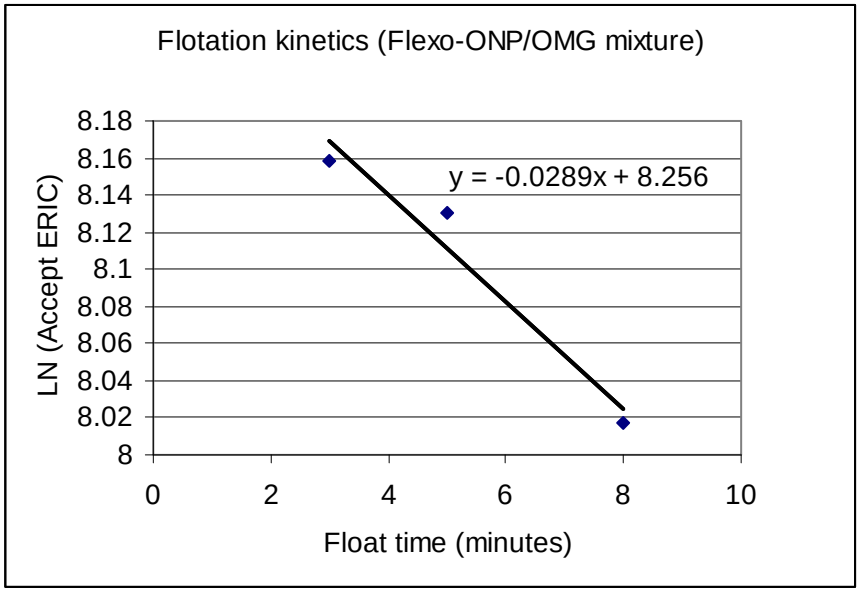

Figure 8-3 Flotation kinetics, natural logarithm of Accept ERIC as a function of time

8.5 Water clarification

The filtrate collected in the screen washing stage can also be recycling to the pulping stage. First though the water is treated. Water clarification methods include dissolve air

flotation, ultra-filtration method. Another method known as electroflotation involves the use of electric field. The efficiency of the water clarification process could be determined empirically. Once the water treatment is complete, it could be used to dilute the thickened stock (obtained from the wash screening stage). This diluted stock could be recycled to a second cycle of treatment. Deinking chemical can be added to the diluted stock prior to introduction to the flotation deinking stage. There could be a third or more stages depending on when the target brightness and ERI value of the deinked pulp (DIP) is achieved. In deinking mills, the DIP target goal is ERIC value of 235ppm. That ERIC value corresponds to a brightness of about 58%. [15]

Table 8-2 ERIC Data: Proposed complete deinking treatment of 100% flexographic ONP

	After pulping (ERIC)	*After flotation (ERIC)*	*After washing (ERIC)*	*After dilution with clarified water(ERIC)*
1st pass	4237	3218	1490	1553
2nd pass	1553	1180	546	500
3rd pass	500	380	176	176

Table 8-2 is example of a complete treatment for 100% flexographic ink. The first pass feed ERIC is 4237 and after treatment, the accept ERIC value is 3218, corresponding to an efficiency, η_E is 0.76, if the first order kinetic is assumed. The ERIC value is 1490 after wash screening, an efficiency of the screen washing 0.46. The filtrate is clarified (treated) with an electric field process, and the clarified water used to dilute the thickened pad formed on the wash screening step. After dilution the resulting suspension is floated again in the first state of

the second pass. Based on the efficiency determined empirically the ERIC values after flotation wash screening and dilution of the thickened pad is estimated.

8.6 Conclusion

Tackling the deinking of 100% flexographic ONP require a multi-process and multi-cycle approach.

The major first step in a deinking operation, pulping, was model Langmuir kinetics. The time constant τ_{esc} and τ_{dep} are a function of the hydrodynamic and colloidal interactions between the ink and fiber. τ_{esc} and τ_{dep} were estimated to be 275s and 600s respectively.

The subsequent flotation deinking step was described using a first order kinetics.

The flotation step is follow by water clarification using electro flotation. The combination of flotation deinking, wash screening and water clarification was able to achieve the target ERIC and brightness of deinked pulp. A final deinked-pulp ERIC of 176 was determined empirically.

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CHAPTER 9 : CONCLUSION

The introduction of flexographic old newsprint into a feedstock drastically reduces the brightness and increases the effective residual ink concentration. Design a deinking facility that can handle an upset caused by the introduction of flexographic ink is important. Understanding the chemical composition and behavior of the ink will help the course of removing it from the flowchart. Pulping is a major stage in the stock preparation for deinking. The behaviors of these flexographic inks are influenced by pulping conditions like pH, temperature, and pulping time. Stock preparation is followed by the actual deinking stage. Deinking could be accomplished by flotation and washing or a combination of both. This study describes a process that incorporates the electric field into the floating deinking process.

Batch deinking was carried out using a laboratory small-scale tank. The electric field voltage was 20-40 volts. For the furnish containing offset ONP, the ISO brightness of the handsheet is 11% higher and the ERIC reduction is 5% greater when an electric field is incorporated into flotation deinking. For the furnish containing 20% flexographic ONP, The bottom of the handsheet shows ERIC reduction of 43% for treatment with electric field, while without electric field, the ERIC reduction is only 5%. At 40% flexo ONP in the furnish, the bottom of the handsheet shows an ERIC reduction of 37% for treatment with electric field, while without electric field the ERIC reduction is only 9%.

In a semi-continuous deinking, the float temperature and solid percent or consistency, electric field, pulping time, type of pulping device, and surfactant type and concentration on deinking efficiency were investigated. The electric field voltage was 750-1500 volts. Flotation deinking efficiency- considering the other variables- with and with electric field is compared; a paired “t test” of the percent reduction in ERIC show statistically significant difference.

Thermogravimetric Analysis was used to corroborate the improved deinking efficiency observed and measured with ERIC.

The deinking selectivity was reported as Z-weighted factor. A 100% flexo-ONP was used to perform this study at two temperature levels, and different surfactant levels in the presence of electric field .The average Z-weighted factor is 18% higher with electric field compared to no electric field

The improved deinking efficiency observed with the introduction of an electric field is ascribed to the small bubble size generated by an electrolysis process and the ability of these bubbles to remove ink, especially flexographic ink. The higher number and surface area of smaller size bubbles improved collision with fine inks and is a possible mechanism behind improved deinking efficiency. The mechanism behind improving deinking efficiency with an electric field is also described as related to the volume of froth rejects during float deinking.

In a deinking mill, water clarification is paramount to a successful operation. A water clarification process that uses an electric field is discussed. The voltage, current, treatment time, ink concentration, and electrode type on water clarification is investigated. The ink concentrations as measured by turbidity, COD, and cationic demand trash is reduced. The degree of decontamination is a strong function of pH and current density. The pH affects the degree of ionization, which is measured by cationic charge demand. At pH 4, the turbidity of the 88 mg/L ink dispersion decreased by 80% and 92% at current densities of 250 mA and 400 mA respectively after 20 minutes of treatment. Also, at pH11, the turbidity of the 88 mg/l ink dispersion decreased by 8% and 41% at current density of 250 mA and 400 mA respectively after 20 minutes of treatment. A direct comparison of copper, aluminum,

stainless steel electrode, shows that their respective decontamination efficiency, reported as the percent change in turbidity, decreases in that order, i.e. 76%, 61% and 4% respectively

The treated water can be used in the deinking operation. In the study, complete treatment is proposed. The flotation deinking and wash deinking followed by a water clarification can be repeated in two or three cycles to achieve target brightness or effective residual ink concentration.

CHAPTER 10 : RECOMMENDATION

The problem of deinking flexographic ink is well documented. In the present, we tackle the problem using a process that incorporates the use of electric field into the flotation deinking process. In addition, we propose treating the filtrate from a wash deinking process so that the water can be used. The water clarification step is critical especially in a close mill operation ("no entry and exit" the water is used and reused in a close system). However, further work can be pursued to improve the use of electric field in flotation deinking and water clarification.

The investigation of how different electrode types and geometries affect flotation deinking as well as water clarification is needed. The effect of electric field on the fiber physical properties needs to be investigated. Physical properties of the deinked pulp are also crucial to a successful deinking operation.

In this study, the electric volts or potential provided by the external power source is only gives information of the difference of potential between the two electrodes. The potential reading is substantially greater than what is needed to drive the electrochemical reactions. Thus, more than one redox reactions could be occurring at the same time. A potentiometer is needed to determine the actual potential at each electrode and to conduct a controlled study of the influence of potential on the various possible redox reactions.

Most of the study has been focused on old newsprint and old magazine paper. A type of waste paper not studied was mixed office wastes, which are papers that were printed with laser printers and copy printers. Laser printers use an electric field process to transfer electrically charged inks from bulk of the toner to the surface of the paper. An investigation of how the electric field in flotation deinking effects the deinking of this electrically charged

toner would be interesting, since toner ink are charge and have larger average diameter of 200 μm.

A membrane reactor could be designed to take advantage of the electrophoresis process (i.e. the movement of charge ink particles due to electric field force), where the membrane can separate the inks from the fiber mixture.

The longer pulping time clearly amplifies the flexographic ink fragmentation and redeposition problem. An investigation of pulping time is significant. For very short pulping time, defibering may not be complete; one could consideration vigorous mixing during the subsequent flotation to complete the defibering process

Washing deinking should definitely be part of the discussion of solutions for flexographic ink. In screen washing, however, the yield loss is high. In the clarification of the subsequent filtrate, a study needs to be carried out to find ways to recover some fines in the filtrate. Electroflotation could help with recovering of these fines.

The flexographic ink is pH responsive. A conventional alkaline pulping and flotation in alkaline conditions followed by a flotation in acidic conditions has been proposed. A treatment can be envisioned where the conventional alkaline pulping is followed by flotation in acidic conditions. The alkaline pulping allows for the easy solubilization of the flexographic ink and detachment from the paper. The acidic condition in flotation reduces the solubility of the flexographic ink and increases its size, which improves the floatability of the ink.

Hydrogen peroxide and sodium hydroxide are core constituents of the deinking chemistry. Often hydrogen peroxide is produce by the electrolysis of a dilute sodium hydroxide solution in specially designed electrochemical cell. As in this current study, a float

cell could be design that incorporates this unique electrochemical cell. If this is fixable, simultaneously deinking and bleaching could be achieved, which would markedly improve accept brightness.

Lastly, the importance of surfactant cannot be over-emphasized. Developing a polymer and/or surfactant chemical system that can selectively increase the hydrophobicity of the flexographic inks and decrease the hydrophobicity of the fiber fines would be a giant step in the right direction. The chemical system should also play an important role in reducing the redeposition and the agglomeration of inks on fiber.

APPENDIX A.

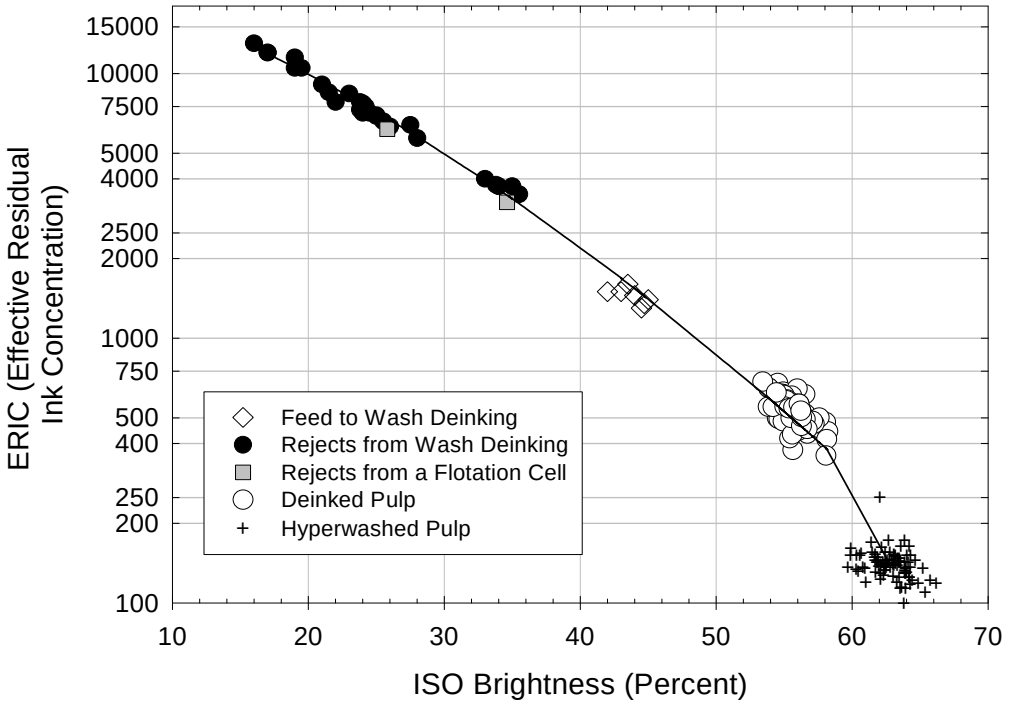

Figure A-1. Relationship of Brightness to ERIC at High Ink Content

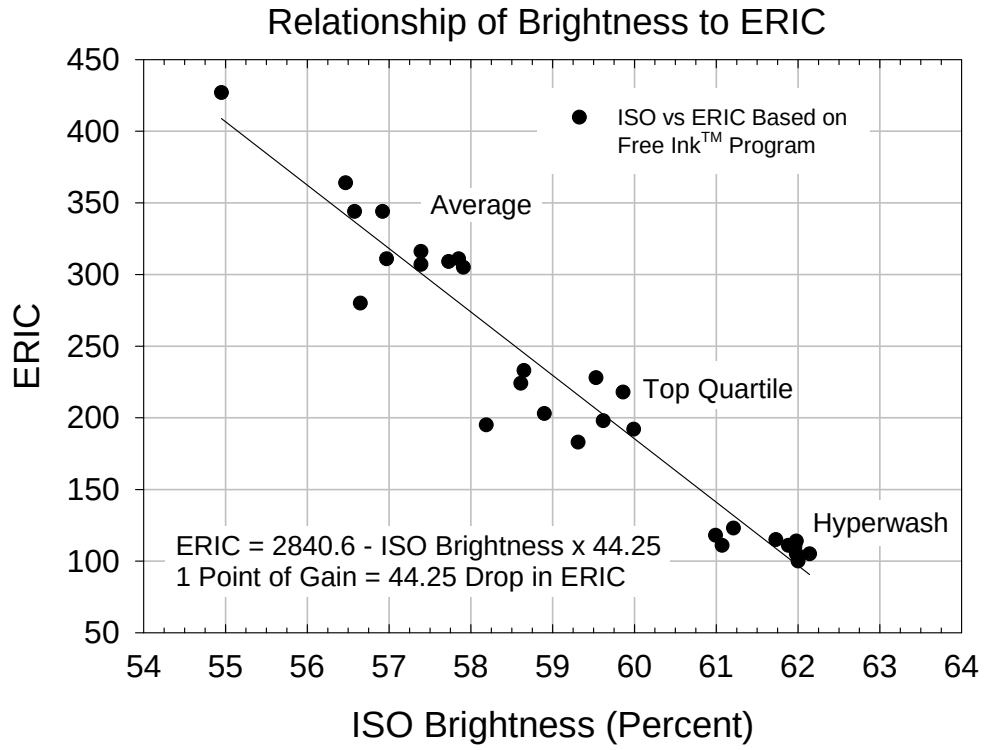

Figure A-2 Relationship of Brightness to ERIC for Deinked Pulp

APPENDIX B.

Table B-1Raw data. 2^3 factorial design, estimated effect calculation

Variable 1	Variable 2	Variable 3	Observation	A	B	C	Estimated effect
-	-	-	a	a'=a+b	a"=a'+b'	A"'=a''+b''	Grand effect= sum of column C/8
+	-	-	b	b'=c+d	b"=c'+d'	B"'=c''+d''	B"'/4
-	+	-	c	c'=e+f	c"=e'+f"	C"'=e''+f''	C"'/4
+	+	-	d	d'=g+h	d"=g'+h'	D"'=g''+h''	D"'/4
-	-	+	e	e'=b-a	e"=b'-a'	E"'=b''-a''	E"'/4
+	-	+	f	f'=d-c	f"=d'-c'	F"'=d''-c''	F"'/4
-	+	+	g	g'=f-e	g"=f"-e'	G"'=f"'-e''	G"'/4
+	+	+	h	h'=h-g	h"=h'-g'	H"'=h''-g''	H"'/4

There are three variables, 1, 2, & 3. For each variable, there are two levels, + for high &- for low. The observation, a, is the response of the system when each variable is at a low level.

Table B-2 Raw data, Pulping time, Temperature and electric field

Flot Feed	*FF-stdv*	*Flot Accept*	*FA-stdv*	*ERIC*	*Flot Feed*	*FF-stdv*	*Flot Accept*	*FA-stdv*	*FA-FF*
4449	118	2676	45	39.9	25.26	0.37	31.94	0.21	6.68
4495	95	2614	52	41.9	25.19	0.25	32.11	0.17	6.92
4301	67	2456	42	42.9	25.70	0.12	33.16	0.14	7.46
4153	83	2281	36	45.1	25.82	0.23	33.75	0.17	7.93
4853	86	3164	35	34.8	22.86	0.19	28.67	0.15	5.81
4997	68	2999	19	40.0	22.34	0.16	29.23	0.11	6.90
5032	72	3182	39	36.8	22.84	0.12	28.99	0.11	6.15
5048	70	2941	27	41.7	22.67	0.21	29.76	0.16	7.10

Table B-3 Calculation of estimated from the observation, percent reduction in ERIC

e.f	*Pulping time(min)*	*Temperature (^oC)*	*% Change in ERIC*				*Estimated effects*
no e.f	5	30	39.9	81.8	169.8	323.1	41.7
e.f	5	30	41.9	88	153.3	14.3	3.575
no e.f	5	43	42.9	74.8	4.2	9.9	2.475
e.f	5	43	45.1	78.5	10.1	-0.1	-0.025
no e.f	20	30	34.8	2	6.2	-16.5	-4.125
e.f	20	30	40	2.2	3.7	5.9	1.475
no e.f	20	43	36.8	5.2	0.2	-2.5	-0.625
e.f	20	43	41.7	4.9	-0.3	-0.5	-0.125

Table B-4 2^3 factorial design of experiment. Feed, Accept and Reject ash

e.f	*Temp*	*pulping time*	*Experiment no*	*Feed ash*	*Accept ash*	*Reject ash*
e.f	30	20	1	0.04569	0.03781	0.22574
no e.f	30	20	2	0.04501	0.03839	0.23482
e.f	43	5	3	0.04624	0.03574	0.23111
e.f	43	20	4	0.04681	0.03739	0.17247
no e.f	43	20	5	0.04561	0.03871	0.17179
no e.f	43	5	6	0.04729	0.03563	0.24449
e.f	30	5	7	0.04645	0.03154	0.25716
no e.f	30	5	8	0.04663	0.03724	0.25152

Table B-5Raw data for 16 experiments.

1ml 30% H_2O_2 and 4ml 10% $CaCl_2$ (10%) was added to each experiment run

Experimental no	*Electric field (volts)*	*NaOH (pH)*	*Consistency (%)*	*Surfactant (µL)*	*Soap (µL)*	*Feed (pH)*	*Pulping study*	*Feed ERIC*	*Feed Brightness*	*Accept ERIC*	*Accept Brightness*	*delta % ERIC*	*delta brightness*	*Solid loss%*
9	0	0	0.5	0	0	8.08	9	2297.55	35.795	1776.35	39.585	22.69	3.79	6.2
10	1000	0	0.5	0	0	7.777	10	2350	35.43	1650.35	40.18	29.77	4.75	3.8
11	0	5	0.5	0	0	9.856	11	2751.6	31.79	2205	35.775	19.86	3.985	4.0
12	1000	5	0.5	0	0	9.828	12	2678.7	32.345	2169.1	35.735	19.02	3.39	2.8
4	0	0	1	0	0	7.564	4	2394.85	34.925	1637.05	40.325	31.64	5.4	7.5
8	1000	0	1	0	0	7.615	8	2351	35.42	1400.7	42.325	40.42	6.905	8.2
3	0	5	1	0	0	9.373	3	2712.65	32.145	1514.95	40.43	44.15	8.285	5.5
7	1000	5	1	0	0	9.763	7	2764.9	32.23	1846	38.03	33.23	5.8	6.6
13	0	0	0.5	10	30	8.004	13	2290.35	35.365	1767	39.14	22.85	3.775	5.8
14	1000	0	0.5	10	30	8.048	14	2302.6	35.465	1733.6	39.46	24.71	3.995	6.1
15	0	5	0.5	10	30	10.097	15	2703.35	32.575	1735.8	39.035	35.79	6.46	4.9
16	1000	5	0.5	10	30	10.134	16	2707.35	32.295	1494.95	40.48	44.78	8.185	7.2
1	0	0	1	10	30	7.979	1	2291.9	35.4	1635.95	40.02	28.62	4.62	9.0
6	1000	0	1	10	30	7.628	6	2412.2	34.765	1614.4	40.455	33.07	5.69	7.6
2	0	5	1	10	30	9.954	2	2635.45	32.74	1421.8	41.38	46.05	8.64	7.4
5	1000	5	1	10	30	10.105	5	2619.25	33.005	1333.35	42.12	49.09	9.115	9.3

Table B-6 16 experiments. Ash fraction in feed, accept and reject

Experiment no	*Feed ash*	*Accept ash*	*Reject ash*
16	0.1203	0.0845	0.5837
15	0.1202	0.0966	0.5757
14	0.1185	0.0917	0.5314
13	0.1206	0.0964	0.5147
12	0.1179	0.1058	0.5300
11	0.1247	0.1057	0.5843
10	0.1198	0.1031	0.5440
9	0.1221	0.0999	0.4558
8	0.1197	0.0819	0.5418
7	0.1211	0.0953	0.4889
6	0.1195	0.0912	0.4622
5	0.1208	0.0775	0.5445
4	0.1242	0.0917	0.5261
3	0.1237	0.0973	0.5796
2	0.1225	0.0851	0.5922
1	0.1180	0.0813	0.4889

Table B-7 Raw data ash fraction. Temp., Surfactant, and E.f.

Temperature	Electric field	Surfactant concentration	feed ash	accept ash	reject ash
25	0	0	0.04425	0.03266	0.15555
25	1.25	0	0.04529	0.02883	0.16770
48	0	10	0.04562	0.03424	0.16690
48	1.25	10	0.04714	0.03074	0.13611
25	0	30	0.04629	0.03603	0.11580
25	1.25	30	0.04561	0.03892	0.15553

1. Solid loss determination

The solid loss in a flotation process is determined from the ash balance of the feed, accept and reject.

$$Yield_{Total} = \frac{Q_{Accept}}{Q_{In}} \qquad \textbf{Equation B-1}$$

$$Yield_{Fiber} = \frac{X_{FiberAccept} Q_{Accept}}{X_{FiberIn} Q_{In}}$$

$$Q_{In} = Q_{Accept} + Q_{\mathrm{Re}\,ject}$$

$$X_{FiberIn} Q_{In} = X_{FiberAccept} Q_{Accept} - X_{Fiber\,\mathrm{Re}\,ject} Q_{\mathrm{Re}\,ject}$$

$$SolidLoss_{Total} = 1 - \left(\frac{\left(X_{\mathrm{Re}\,ject} - X_{in}\right)}{\left(X_{\mathrm{Re}\,ject} - X_{Accept}\right)} \right) \qquad \textbf{Equation B-2}$$

$$SolidLoss_{Fiber} = 1 - \left(\frac{\left(1 - X_{Accept}\right)\left(X_{\mathrm{Re}\,ject} - X_{In}\right)}{\left(1 - X_{In}\right)\left(X_{\mathrm{Re}\,ject} - X_{Accept}\right)} \right) \qquad \textbf{Equation B-3}$$

where X_{Accept}, X_{In}, X_{Reject}, are the fractions of ash by weight in the flotation cell accepts, feed, and rejects samples, respectively

2. The percent consistency of the specimen is:

% consistency =

100*([Weight of dry pad & filter paper - Weight of filter Paper]/Weight of original pre-filtered sample) **Equation B-4**

3. Free Ink

% Free Ink = 100 x ([ERIC Normal Pulp - ERIC Hyperwashed Pulp]/ERIC Normal Pulp)

4. **Z weighted factor**

$$Z\ factor\quad weighted\quad ERIC\ reduction\quad = \frac{(Feed\quad ERIC\quad -\ Accept\quad ERIC\ )^2}{Feed\quad ERIC\quad *\ (\%)\ Solid\quad loss}$$

$$Z\ factor\quad = \frac{(Feed\quad ERIC\quad -\ Accept\quad ERIC\ )}{Feed\quad ERIC\quad *\ (\%)\ Solid\quad loss}$$

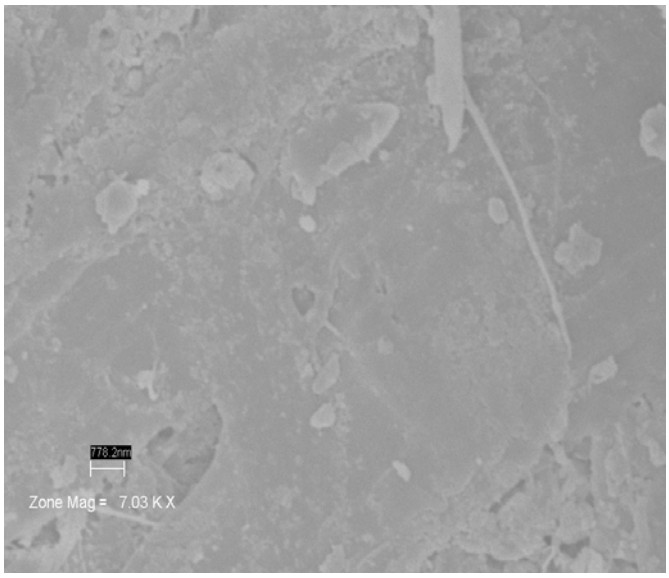

Figure B-1Figure 4 8 SEM image of accepts. Electric field is not used in deinking

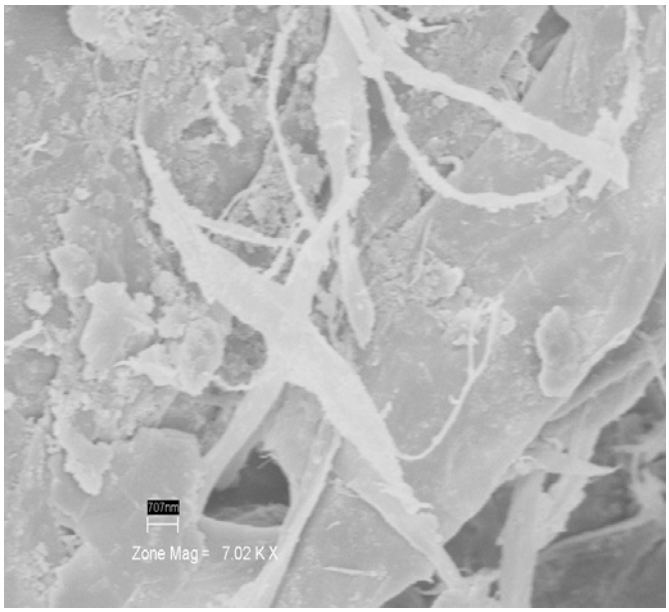

Figure B-2 SEM image of accept obtained from deinking with electric field

Table B-8Calculation of ink on fiber (g) using filtrate turbidity data

Time (sec)	*Turbidity (FAU) spec 4100*	*mg/ml*	*mg in 200ml*	*mg of ink/ g of fiber*	*if 3g of fiber contain, x amount of ink in solution, then 50g of fiber will contain (50* x /3)g ink the filtrate*	*ink on fiber (g)*
0	50	0.000136	0.00002726	0.00861416	0.000430784	12.95316
30	1347	0.029838	0.00596752	1.88573632	0.094303413	11.07603
60	1873	0.041883	0.0083766	2.6470056	0.132373578	10.31476
90	3392	0.076668	0.01533362	4.84542392	0.242313843	8.116346
150	5394	0.122514	0.02450278	7.74287848	0.387212073	5.218892
270	5500	0.124941	0.02498826	7.89629016	0.394884008	5.06548
	9000	0.205091	0.04101826	12.96177	0.68363	

First using model flexographic ink, the calibration curve of ink concentration and turbidity is determined (Figure B-1)
50g of newsprint is pulped at 6% consistency
During pulping of the newsprint, 50 ml of sample (or 3g dry weight) are collected at different intervals
Then the 50ml sample (diluted to 200 ml) is passed through a screen to thicken it and the water filtrate is collected and turbidity measured. The turbidity of the sample collected at 30 sec was 1347 FAU.

Then, from the turbidity and calibration curve, the concentration (mg/ml) is determined (Figure B-1). Turbidity of 1347 FAU corresponds to an ink concentration of 0.030 mg/ml
Then the amount of the ink (mg) in 200 ml of filtrate is determined. E.g. 0.030 (mg/ml) * 200 ml equals 0.0060 mg
The consistency of the sample from which the filtrate was collected was 1.582%.
Then the amount of ink (mg) per gram of fiber is determined. E.g. 0.030 (mg/ml) /1.582% fiber consistency gives 1.89 mg of ink/g of fiber
Then a maximum turbidity of 9000 FAU, this is an estimated of what the turbidity of the filtrate would be if all the inks are separated from the fiber as pulping is continued indefinitely. The ink on fiber at a given pulping time is difference between the maximum ink of fiber and the ink in the filtrate
If 3g of fiber contain, x mg amount of ink in 200 ml solution, then 50g of fiber will contain ((50*x mg)/3) g ink the filtrate

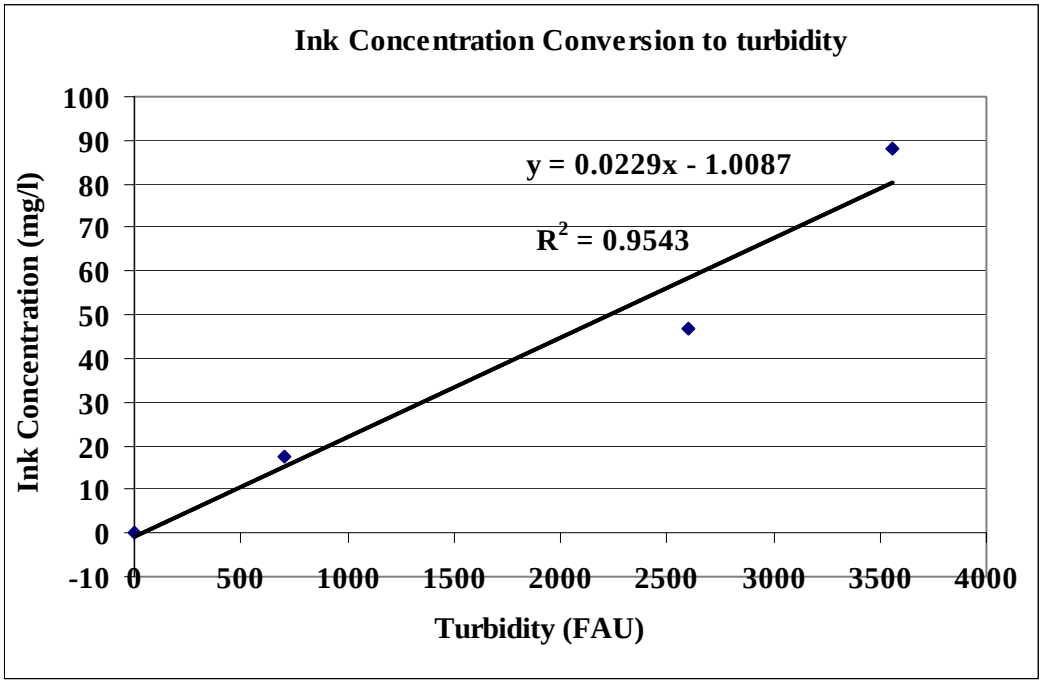

Figure B-3 Calibration curve ink concentration in filtrate

APPENDIX C.

SURFACTANT

- ***Floatsan 209*** is made by BASF. The surfactant chemistry is proprietary. However it a non-ionic surfactant with no phenol groups. Most non-ionic surfactants are ethylene oxide and propylene oxide (PO) copolymer, Alcoxylated fatty alcohols or Alcoxylated fatty acids.

- ***DowFAX 3B2*** is made by DOW. It main ingredient is alkyldiphenyl oxide Disulfonate. The other component is C_{10}-alpha olefin. It is anionic surfactant

- ***EKA RF 4283*** is made by EKA chemicals. It is a non-ionic surfactant. It cloud point is greater than $75^{o}C$

- ***EKA RF 4031*** is made by EKA chemicals. It is soap. Soaps are considered as anionic surfactant. Tallow fatty acids. The hydrophilic group is likely carboxylates

Table C-1Conductivity data from electroflotation treatment of flexographic ink (chapter 7)

pH	Current (mA)	Treatment Time	*Conductivity* 0	20	30
			aluminum cathode @ 88mg/l of ink		
4	400 mA		0.184	0.1716	0.1711
11			0.515	0.49	0.431
7			0.1427	0.1278	0.1375
9			0.211	0.181	0.1662
4	250 mA		0.1745	0.1707	0.1756
11			0.458	0.644	0.581
7			0.1414	0.14	0.1375
9			0.211	0.206	0.26
			copper cathode @ 44mg/l of ink		
4			0.1832	0.1787	0.1579
11	250 mA		0.824	0.81	0.805
7			0.1538	0.1418	0.1494
9			0.1434	0.1504	0.1463
4	400 mA		**0.1832**	**0.1787**	**0.1579**
11			0.167	0.1508	0.162
7			0.1434	0.136	0.1324
9			0	20	40
			aluminum cathode @ wash filtrate containing		
4			0.26	0.312	0.3
7	125 mA		0.215	0.24	0.223
9			0.197	0.193	0.196
11			1.617	1.682	1.66
4	250 mA		0.298	0.313	0.285
7			0.232	0.224	0.222
9			0.191	0.193	0.206
11			1.05	1.456	1.261